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**Phosphorus in UK Rivers: The Impact of Urban  
Waste Water Treatment Directive**

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**Master of Science by Research**

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**2016**



## **Abstract**

Excessive phosphorus levels leading to eutrophication in natural waters as a result of growing population, urbanisation and intensified agriculture has long been a major environmental concern at a global scale. Many remediation strategies and actions have been undertaken since the implementation of Urban Waste Water Treatment Directive (UWWTD) in 1992. The UWWTD was implemented to reduce direct phosphorus inputs into rivers from effluents of sewage treatment works. Nevertheless, the long-term outcomes and effectiveness of these actions still remain unknown. An understanding of the prospective results and effectiveness of these implementations is only possible with a retrospective analysis of riverine phosphorus dynamics.

Therefore, this thesis explored the evolution of P concentration and flux from across the UK with datasets available from 230 river sites between the period of 1974 and 2012. These datasets were examined with the purpose of detecting the traces of the events that are likely to be governing the changes in phosphorus levels over this time period i.e. the implementation of the UWWTD. Trend and change point analyses conducted on Total reactive phosphorus (TRP) and Total phosphorus (TP) data indicated that the concentrations and fluxes have been declining since the mid-1980s correlating with declining phosphate-fertilizer usage. The sites with the largest declines were from the Midlands and South East regions of England, whereas Scotland has seen almost no change. Significant step changes were encountered in most of the TRP concentration records, and most of these step changes were detected in the period 1993-1997 suggesting that the UWWTD was the key factor leading to these step changes. To validate this hypothesis, Principal component analysis (PCA) was conducted to be able to track down the urban source contributor. Water quality (TRP, BOD, Suspended solids, Nitrate concentration and Conductivity) data from 5 example sites were analysed however, in none of the case examples was there an explicit principle component that could be construed with an urban or any other source contributor. Therefore, the PCA technique was not found to be a suitable technique to analyse this type of datasets.

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## **Chapter 1:**

### **Introduction**

#### **1.1. Overview and Rationale**

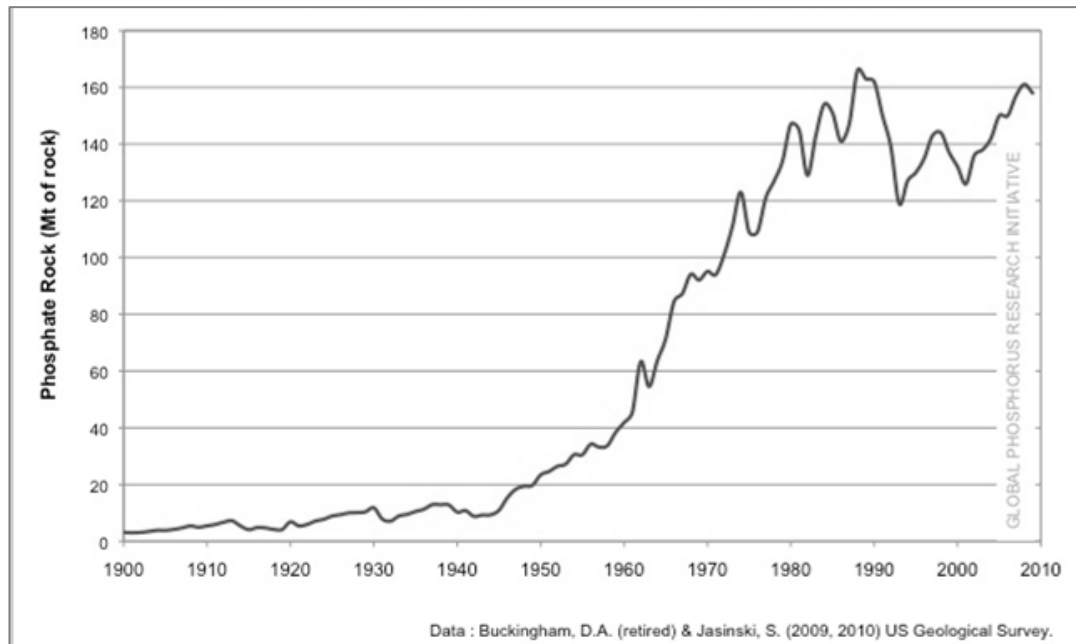
Over the last century, urbanisation and industrialisation have led to masses of carbon being moved from underground to the atmosphere, devastating the climate to meet the growing need for energy. Intensified agriculture has led massive amounts of nitrogen to be pulled from the atmosphere and moved to the lands, rivers and forests, ruining the balance of many ecosystems in order to meet the needs of a growing population. Another essential nutrient whose global cycle has been extensively altered is phosphorus and it has received much less press than carbon and nitrogen. Excessive levels of phosphorus is one of the sources of environmental pollution, and ironically, mineable resources of this element are limited. There is an urgent need to restore the broken cycle of phosphorus (Elser & Bennet, 2011).

##### **1.1.1. Phosphorus and its role**

Phosphorus (P) is ranked as the eleventh 11<sup>th</sup> most abundant element in Earth's crust and geochemically classed to be a trace element (Holtan, et al., 1988). As an essential nutrient for the metabolic functioning of all forms of life, it plays a

crucial role in controlling productivity in both terrestrial and aquatic ecosystems (Correll, 1998; Caraco, 2009). Phosphorus is a critical factor in crop yields and accordingly, it is an important part of modern food production.

Use of phosphate rock for commercial production purposes started in the 19<sup>th</sup> century with mining works in Spain, followed by England and France (Holtan, et al., 1988). Shortly after, worldwide phosphate rock production increased over 16 fold in the period between 1940 to 1990 (Figure 1.1). Today, approximately 90% of phosphate rock extraction is for food production and crop nutrition purposes while the remainder is for industrial purposes. Shortages of phosphate rock would have great impacts on inorganic fertilizers and thus for production of crops, which could eventually jeopardise World food security (Amundson, et al., 2015; Kroiss, et al., 2011). Some studies have reported that the life time of phosphorus reserves is 50 to 100 years (Cordell, et al., 2009; Rosmarin, 2004), conversely, others have suggested life times up to hundreds of years (Van Vuuren, et al., 2010; EFMA, 2000). Debates on depletion of phosphorus are still ongoing with different estimates of phosphate rock reserves.



*Figure 1.1 World phosphate rock production between the years 1900 – 2009 (Adapted from (Global Phosphorus Network, n.d.))*

### **1.1.2. Phosphorus as an important contributor of Eutrophication**

Excessive levels of nutrients in natural waters has led to eutrophication which has become a major environmental concern at the global scale (Hecky & Kilham, 1988; Mainstone & Parr, 2002). Eutrophication causes serious degradation in the aquatic ecosystem and lowers biodiversity with the excessive development of algal blooms and growth of large rooted plants (macrophytes) (Figure 1.2) resulting in hypoxia (Liu, et al., 2012; Hilton, et al., 2006). In particular, rivers have been extensively affected because of their sensitivity to the changes in land use and management and extensive exploitation of these waters for many uses from water supply to waste disposal (Malmqvist & Rundle, 2002).



*Figure 1.2 Examples of different stages of eutrophication in rivers (Adapted from Hilton, et al., 2006)*

### **1.1.3. Sources of Phosphorus loadings into rivers**

As the primary limiting nutrient in most waterbodies, a great deal of eutrophication management studies have focused on phosphorus loadings. There is a variety of potential pollutant sources for rivers as given in Table 1.1. The most common anthropogenic sources for phosphorus loads into rivers are generally segregated to two classes; point sources which are dominated by sewage and industrial effluents, and diffuse sources such as agricultural loads delivered with soil run-off (Neal, et al., 2004). Point sources are localized and thus easier to monitor whereas diffuse sources are much more difficult to monitor and control. Contributions of these sources differ depending on the watershed characteristics,



local population, land use etc. (Smith, et al., 1999). Point sources usually contain a high proportion of soluble and more biologically available phosphorus (Jarvie, et al., 2006). Unlike point sources, phosphorus in diffuse sources are generally in particulate forms (P sorbed to soil particles) (EA, 2015). Contribution of agricultural diffuse P loadings (i.e via farmyard run-off, pig slurry etc.) is substantially higher than urban sources such as STW effluent, road run-off and septic effluent along with Nitrate (N) and Suspended Solids (SS) loadings (Edwards & Withers, 2008). Accordingly, containing higher amount of nutrients, diffuse sources such as agricultural run-off have higher Biological Oxygen Demand (BOD) than point sources like sewage effluent.

Phosphorus in wastewaters is mainly generated from human sources, cleaning products such as detergents and industrial effluents (EA, 2012). Contribution of human excretion to P inputs in sewage effluents is approximately 75%, whereas detergents comprises around 25% of the P source; and many brands have started to reduce phosphate contents in laundry detergents lately (Richards, et al., 2015). However, even if the phosphates were entirely removed from the cleaning products, substantial amounts of human sourced P inputs will remain (Scholz, et al., 2014). Wastewater effluents generally have high amounts of dissolved salt from domestic sewage. Electrical conductivity is a good indicator of water salinity (Morrison, et al., 2001), therefore high conductivity readings can be used as an indicator of human activity (urban point source).

*Table 1.1 Sources of pollution and potential discharges into rivers (Adapted from Foundation of Water Research, 2005)*

<b>Examples of Sources of Pollution</b>	<b>Point or Diffuse Source</b>	<b>Potential Pollutant</b>
Effluent discharges from sewage treatment works	Point source	Nitrogen (N), Phosphorus (P), persistent organic pollutants, pathogens, solids, litter
Industrial effluent discharges treatment	Point source	N, oxygen-depleting substances and a broad spectrum of chemicals
Industrial processes	Point Source	Broad spectrum of chemicals released to air and water
Oil storage facilities	Point source	Hydrocarbons
Urban stormwater discharges	Point source - arising from storm water runoff (from paved areas and roofs in towns and cities) entering the sewer network	N, P, oxygen-depleting substances, heavy metals, hydrocarbons pathogens, persistent organic pollutants, suspended solids, settleable solids, litter
Landfill sites	Point source	N, ammonia, oxygen-depleting substances, broad spectrum of chemicals
Fish farming	Point source	N, P, oxygen-depleting substances, pathogens
Pesticide use	Diffuse source	Broad spectrum of chemicals
Organic waste recycling to land	Diffuse source	N, P, pathogens
Agricultural fertilisers	Diffuse source	N, P
Soil cultivation	Diffuse source	Soil, N, P
Power generation facilities	Diffuse source	N, Sulphur
Farm wastes and silage	Point/Diffuse source	N, P, oxygen-depleting substances, pathogens
Contaminated land	Point/Diffuse source	Hydrocarbons, organic chemicals, heavy metals, oxygen-depleting substances
Mining	Point/Diffuse source	Heavy metals, acid mine drainage
Leaking pipelines	Point/Diffuse source	Oil, sewage

A portion of P loadings from diffuse and point sources within a watershed can accumulate in soils and aquatic sediments along transport pathways and accumulated P can be remobilized or recycled, acting as a continuing source of P transport with residence times of years to decades (Sharpley, et al., 2014). This has been referred to as “legacy-phosphorus” and it causes considerable delay in recovery of water quality impairment (Powers, et al., 2016).

#### **1.1.4. Technologies for Phosphorus Removal and Recovery**

The European Union’s Urban Waste Water Treatment Directive (UWWTD - European Commission, 1991) was brought in to restrict the pollution of natural waters by wastewater including limiting urban wastewater as a source of P. As a result of the UWWTD numerous actions have been executed for the reduction of direct phosphorus inputs into rivers from effluents of sewage treatment works (STW - Defra, 2002; Neal, et al., 2010a). There is a wide range of technologies both established and under development to reduce/recycle P in wastewaters. These technologies are summarized in Table 1.2. Outputs of each process contain different forms of P such as calcium phosphates, metal bound phosphates, biologically bound phosphates etc. which will affect the chemical composition of the resulting catchment.

Table 1.2 Phosphorus removal and recovery technologies (Adapted from Morse, et al., 1998)

Technology	Objective	Process summary	Main input	Auxiliary inputs	Main output	P form/content
Chemical precipitation	Phosphorous removal	Addition of metal salt to precipitate metal phosphate removed in sludge	Wastewater (primary, secondary, tertiary, or sidestream)	Fe, Al, Ca May require anionic polymer	Chemical sludge	Mainly chemically bound as metal phosphate
Biological phosphorous removal	Phosphorous removal (may also include nitrogen removal)	Luxury uptake of P by bacteria in aerobic stage following anaerobic stage	Wastewater (primary effluent)	May require external carbon source (e.g. methanol)	Biological sludge	Phosphorous biologically bound
Crystallisation (DHV Crystalactor™)	Phosphorous removal recovery	Crystallisation of calcium phosphate using sand as a seed material	Wastewater (secondary effluent or sidestream)	Caustic soda/milk of lime, sand; may need sulphuric acid	Calcium phosphate, sand	Calcium phosphate (40%-50%)
Advanced chemical precipitation (HYPO)	Phosphorous and nitrogen removal	Crystallisation of phosphorous/organic matter and hydrolysis to give carbon source for N removal	Wastewater (primary influent)	Polyaluminium chloride (PAC)	Chemical sludge	Chemical sludge
Ion exchange (RIM-NUT)	Fertiliser (struvite) production	Ion exchange removes ammonium and phosphate which are precipitated	Wastewater (secondary effluent)	H <sub>3</sub> PO <sub>4</sub> , MgCl, NaCl, NaCO <sub>3</sub> , NaOH	Struvite (MgNH <sub>4</sub> PO <sub>4</sub> )	Phosphate slurry
Magnetic (Smit-Nymegen)	Phosphorous removal	Precipitation, magnetite attachment, separation and recovery	Wastewater (secondary effluent)	Lime, magnetite	Primarily calcium phosphate	Calcium phosphate
Phosphorus adsorbents	Phosphorous removal	Adsorption and separation	Wastewater	NA	No information	Calcium phosphate
Tertiary filtration	Effluent polishing	Filtration	Secondary effluent	Media	Tertiary sludge	Insoluble phosphate
Sludge treatment	Sludge disposal	E.g. sludge drying, reaction with cement dust	Sludge	Depends on process	Soil conditioner	Dry granule, low in P
Recovery from sludge ash	Phosphorous recovery	Extraction from sludge ash	Sludge ash from biological removal	NA	NA	NA

### **1.1.5. Measures and implementations to reduce phosphorus inputs in the UK**

Following the UWWTD, European Union introduced the Water Framework Directive (WFD) (Council of European Communities, 2000) to accomplish sustainable and improved water quality in a range of waterbodies and phosphorus was indicated as one of the main pollutants with an emphasis on eutrophication sensitive areas defined as part of implementing the UWWTD. With respect to the UK, the Dept of Environment, Food & Rural Affairs (DEFRA) report that there are 588 sensitive areas in the UK made up of 19466 km of rivers and canals; and 2737 km<sup>2</sup> of surface area in total (Defra, 2012). The targets for remediation of sensitive areas and elimination of eutrophication was to reduce annual average SRP concentration in other water bodies change to between 0.02 mg P/l and 0.12 mg P/l (SRP is soluble reactive phosphorus; can also be referred as orthophosphate or total reactive phosphorus - Neal et al., 2010b). The characteristic alkalinity of the catchment is used to determine were in the acceptable range the SRP concentration should be (WFD UK TAG, 2008). Under the terms of UWWTD, sewage treatment works of <10000 population equivalent (p.e.) (unit defined in the directive for assessment of polluting potential of effluents, does not refer to population of communities; Defra, 2012) were required to install a P-stripping unit (as tertiary treatment) (Ferrier & Jenkins, 2009). STWs were also demanded to either meet the specified concentration limits for P in the final effluent; defined as 2 mg/l for 10,000 to 100,000 p.e. and 1 mg/l for over 100,000 p.e., or eliminate 80% of the incoming P (Kinniburgh & Barnett, 2010).

## **1.2. Review on UK phosphorus levels**

The UK lowlands have large population densities and thusly, the lowland rivers are highly vulnerable for P-sourced eutrophication (Neal, et al, 2010a). A study by Jarvie et al. (2006) among 54 monitoring sites of UK lowland catchments investigated the relative contribution of point and diffuse P sources and pointed out that even in rural areas with highly intense agricultural P loadings, point P sources (wastewater) surpasses the diffuse sources and deliver a much greater risk for river eutrophication. White and Hammond (2007) estimated a total SRP load of 47 ktonnes/yr with 78% household, 13% agriculture, 4% industry and 6% background contributions; and a total TP load of 60 ktonnes/yr with 73% household, 20% agriculture, 3% industry and 4% background contributions in Great Britain catchments. Another study by Neal et al. (2010b) upon 9 major UK rivers including their 26 tributaries submitted similar results pointing out the effluent sources. In the corresponding study, the data of different forms of phosphorus such as SRP, TDP, TP, DHP and PP were analysed along with effluent tracers (boron and sodium) and SRP was found to be dominant indicating sewage sources.

UK has accomplished considerable progress on P remediation, however it still falls behind other WFD members states such as Denmark, Sweden, Finland, and the Netherlands where whole territories have been treated as sensitive areas, and also a large proportion of the countries like Germany and France have been designated the same way (Mainstone & Parr, 2002; IEEP, 1999). By 2002, only 2% of the STWs in the UK had P-stripping installations by the year 2002 (Foy, 2007). Muscutt and Withers (1996) carried out a study among 98 rivers in England and Wales, and

reported that 80% of the rivers were failing a target limit of 0.1 mg/l mean orthophosphate concentration (DoE, 1993). However, UK has increased investment and accelerated implementation of the UWWTD on STWs in the last decade (Bowes, et al., 2010). According to the statistics of Defra (2012), investments for the sewage treatment services in England were almost doubled from £9600 M in the period 1990 - 2000 to £16100 M in the years between 2000 – 2015; with a total investment of £39126 M on STWs overall in the UK for the years between 1990 – 2015. These actions started paying off with considerable reduction of phosphorus concentrations in many UK rivers (Kinniburgh & Barnett, 2010; Bowes, et al., 2009; Neal, et al., 2010c). Nevertheless, the extent of riverine phosphorus remediation that is required for a desired level of ecological recovery and also the results of the implementations in the long run remain unknown (Bowes, et al., 2010).

### **1.3. Aims and Objectives**

The objective of this study is firstly to reveal phosphorus dynamics in rivers at a national scale by analyses on the concentration and flux data of Total reactive phosphorus (TRP) and Total phosphorus (TP) from 230 UK monitoring sites. Trend and change point analyses were used to flag descriptive features of the catchments which would accordingly help us to track down the processes and events governing P dynamics, i.e. implementation of the Urban Waste Water Treatment Directive (UWWTD). The second chapter aims to produce a better understanding of the underlying source contributors of riverine phosphorus levels via case examples (River Irwell, Tern, Cuckmere, Otter and Carnon) representing various catchment

characteristics that were deducted using the information obtained from the first chapter.



## **Chapter 2:**

### **TRP and TP Concentration and Flux from the UK**

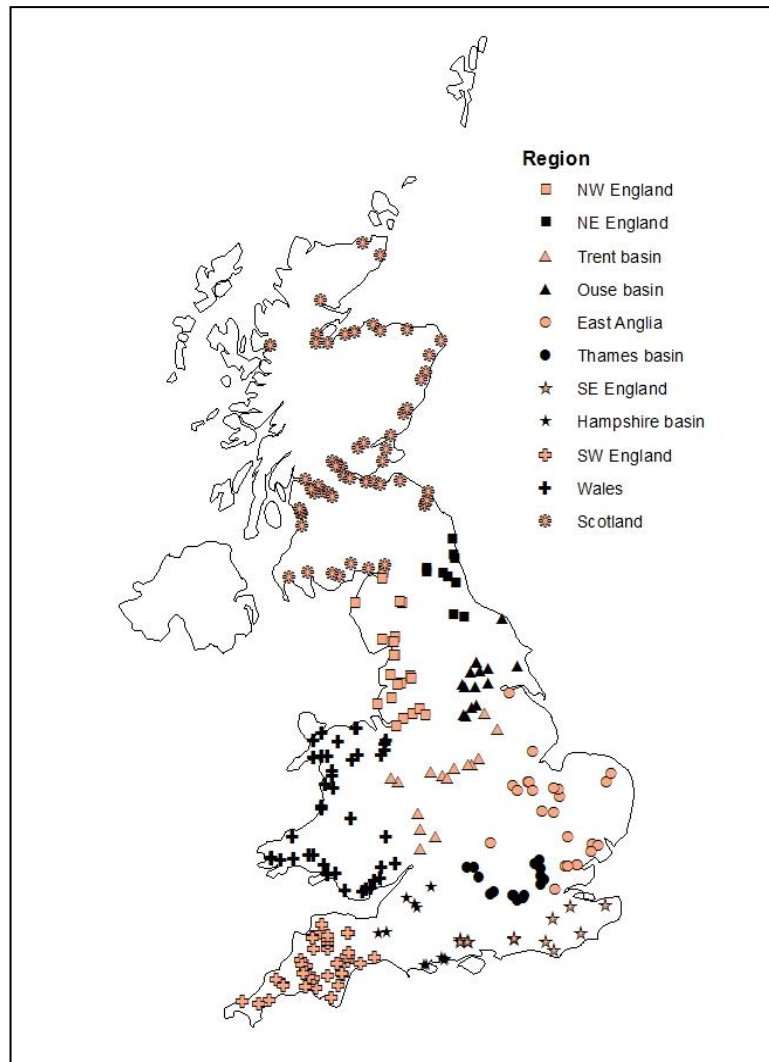
#### **2.1. Introduction**

As it was outlined in Chapter 1, phosphorus linked eutrophication still remains as an important environmental concern at global scale. Targeting the problem, many phosphorus remediation strategies have been implemented, yet an understanding of the outcomes and effectiveness of these implementations needs a further comprehension on the evolution of the riverine phosphorus. Therefore, this chapter explores the national P concentration and fluxes from the UK rivers with datasets available from the period between 1974 and 2012. The main purpose of this chapter was to detect the traces of the events that are likely to be governing the changes in phosphorus levels over this time period, i.e. the implementation of the Urban Waste Water Treatment Directive (UWWTD).

## **2.2. Methodology**

### **2.2.1. Study Sites**

This study used datasets obtained from Harmonized Monitoring Scheme (HMS - Bellamy & Wilkinson, 2001). HMS is a long-term river quality monitoring programme established in 1974 by the Department of Environment (DoE) and has been administrated by the Environment Agency since 1998 (DEFRA, n.d.). The programme contains 270 monitored sites, however data records of 230 HMS sites were suitable for this study. Of these 230 sites; 56 sites are located in Scotland and 174 sites are located in England and Wales (Figure 2.1). No data were available from Northern Ireland, therefore this study was restricted to Great Britain (GB) rather than the entire United Kingdom (UK). For inclusion to the monitoring programme, locations at the tidal limits of main rivers with an annual discharge higher than 2 m<sup>3</sup>/s; or at the tidal limits of any significant tributaries with average annual discharge above 2 m<sup>3</sup>/s were selected. With this criteria, a good spatial coverage on the coast of England and Wales was achieved. However, in Scotland the same extent coverage is not achieved because many of its west coast rivers are too small for inclusion.



*Figure 2.1 Location of HMS monitoring sites used in the study*

Four determinants within the database maintained by the HMS programme were of particular interest for this study: total reactive phosphorus concentration (TRP – mg P/l); total phosphorus concentration (TP – mg P/l); instantaneous flow (m/s) and daily average flow (m/s). Due to the methodology used within the HMS monitoring programme (Simpson, 1980; DoE, 1972) the entries listed as orthophosphate concentration should be considered as TRP, since the methodology for orthophosphate measurement is based on colorimetric analysis of molybdate-

reactive P on an *unfiltered* sample, and thus contains orthophosphate, and other easily-hydrolysable P fractions in both dissolved and particulate phases (Jarvie, et al, 2002). For the total phosphorus measurement, there is an additional acid-persulphate digestion step before the colorimetric analysis (DoE, 1972). The number of TP data available for analysis was much less than TRP data records.

In this study, both concentration and flux of TRP and TP were considered. Due to different monitoring agencies in charge, sampling frequencies and length of records varied between the sites. The length of records available for the study was from 1974 to 2012. Annual data were rejected at any site within any catchment where there were fewer than 12 samples in that year with the samples in separate months ( $f < 12$ ); in this way a range of flow conditions would be sampled. Therefore, only 230 of the 270 sites that were monitored within the HMS could be included in this study.

Flux calculations were carried out using a method proposed by Worrall et al. (2013). The method is based on the nature of the sources of variation within the flow and solute datasets and is a very simple method with a very low bias (8% for  $f = 1$  per month) and a high accuracy (2% at  $f = 1$  per month). The fluvial flux of a solute is estimated by the equation:

$$F = KE(C_i)Q_{total} \quad (2.1)$$

where:  $Q_{total}$  = the total flow in a year ( $m^3/yr$ );  $E(C_i)$  = the expected value of the sampled concentrations (mg/l); and  $K$  = constant for unit conversion (0.000001 for flux in tonnes). For the best results, the expected value of sampled concentration was based upon expected value of a gamma distribution. Flux calculations were made for both TRP and TP records of each HMS site, where sampling frequency criteria was met and the total flow per year could be estimated from daily flow measurements.

### **2.2.2. Analysis of Variance (ANOVA) and Covariance (ANCOVA)**

Analysis of variance (ANOVA) is a statistical technique consisting of a set of models used to identify whether various factors (independent variables) have significant influences upon a continuous response variable (dependant variable). For this purpose, ANOVA tests the factor means to identify if they are significantly different for the given dependant variable. The term “factor” has a number of definitions both in statistics and in other subjects, however in ANOVA modelling, a “factor” is defined as a categorical variable (i.e. non-numeric) representing the experimental/observational conditions or controlled effects. An ANOVA can be extended to ANCOVA by including one or more continuous variables referred as “covariates” that predict the response variable. Unlike factors, covariates are not involved in manipulation of experimental/observational conditions, yet they have influence on the outcome as they covary with the dependant variable. The purpose of including covariates in analysis of variance is to improve accuracy of the model by reducing the within-group error variance and by elimination of confounding effects.

In this study, analysis of variance was implemented with a General linear model (GLM) approach using the commercially available MINITAB v17 statistical software package. The ANOVA and ANCOVA were used to test the difference between monitoring sites across time. Hence, two factors referred as site and year were considered in the analysis. Site factor had 230 levels representing each monitored site and the year factor had 39 levels; one for each for the study period of 1974 – 2012. Analysis of variance was repeated using the water yield (annual average flow) as the covariate for each site (ANCOVA).

The ANOVA assumes that each population is normally distributed, therefore, normality of the datasets were checked prior to analysis using the Anderson-Darling test (Anderson & Darling, 1952). When any non-normality was found, the data (or covariate) were log-transformed before implementation of ANOVA/ANCOVA and no further transformation was found to be required. The results are expressed as least square means (or marginal means) as they are the means controlled for all the factors and covariates. All results are reported at a significance level of  $p < 0.05$  (95% confidence interval).

The proportion of variance, or in other words the magnitude of the effect of each factor and covariate, was estimated by generalized omega square ( $\omega^2$ ) statistics (Olejnik & Algina, 2003). It is a different statistics than ANOVA's coefficient of determination ( $R^2$ ) that only explains the total variance in a model and does not give information any information of individual contribution of factors to the variance.

Therefore,  $R^2$  and  $\omega^2$  results will not be the same. The method for calculation of the omega squared ( $\omega^2$ ) statistic is outlined below:

$$\omega^2 = \frac{(S_{eq}SS_a - d_{fa} \times Adj MS_{error})}{(S_{eq}SS_{total} + Adj MS_{error})} \quad (2.2)$$

where:  $a$  represents factor or covariate  $a$ ;  $S_{eq}SS_a$  is the sequential sum of squares for factor/covariate  $a$ ;  $d_{fa}$  is the degrees of freedom for the factor/covariate;  $Adj MS_{error}$  is the adjusted mean square error and  $S_{eq}SS_{total}$  is the sequential sum of squares for the overall model.

### 2.2.3. Time Series and Trend Analysis

The main purpose of time series analysis on hydrological data is to designate trends and changes for understanding the underlying processes such as climatic changes or anthropogenic impacts on various water bodies. Changes in hydrological time series can occur in different ways such as; gradual increase or decrease (positive or negative trends), step changes (abrupt changes in the series) and/or more complex forms of change. Gradual changes are generally addressed to certain gradual causative changes such as urbanisation, climate change etc., whereas step changes are caused by sudden alterations creating a large impact on the series.

There are many complex approaches for detection of trends in time series, however due to the large number of sites and datasets involved in this study, a

detailed trend analysis for each individual site was not feasible. Instead, trend analysis was used as a preliminary tool to obtain general descriptive information (positive, negative trends, or no trend) about each catchment, therefore it was performed simply by using linear regression approach. Only the sites with at least 20 years of data between the study period of 1974-2012 were subjected to trend analysis for detection of trends in the time series of annual average concentration and flux data of TRP and TP. Also, a further trend analysis was performed on the last decade of the study period with the sites having 8 or more years of records between the years 2003-2012.

#### **2.2.4. Change Point Analysis**

Change point techniques are used to detect abrupt shifts on the structural pattern of a time series by determining whether there is step causing a change or not, using a decision rule based on the statistical significance of the step change. In this study, preliminary visual inspection on the time series of the data suggested that there were large step changes present in the series. To detect and measure the magnitude of these suggested step changes in flux and concentration time series of TP and TRP, a non-parametric method Pettitt's test (Pettitt, 1979) was implemented.

The Pettitt's test uses rank based Mann-Whitney statistics  $U_{t,N}$  comparing two independent sample sets  $x_1, x_2, \dots, x_t$  and  $x_{t+1}, x_{t+2}, \dots, x_N$  to test whether these sample sets are from the same population. The test statistic  $U_{t,N}$  is calculated as follows:



$$U_{t,N} = U_{t-1,N} + \sum_{j=1}^N \text{sgn}(x_t - x_j) \quad \text{for } t = 2, \dots, N \quad (2.3)$$

$$\text{and } \text{sgn}(x_t - x_j) = \begin{cases} 1, & x_t > x_j \\ 0, & x_t = x_j \\ -1, & x_t < x_j \end{cases} \quad (2.4)$$

The step change is defined where  $U_{t,N}$  has the maximum value,  $K_n$ :

$$K_n = \text{Max}|U_{t,N}| \quad (2.5)$$

The significance level of the step change is approximately:

$$P = \exp\left(\frac{-6(K_n)^2}{n^3 + n^2}\right) \quad (2.6)$$

An enhanced probability estimation was suggested by Wilks (Wilks, 2006) for joint evaluation of repeated test results, as in the case of Pettitt's test, otherwise, familywise error (false detection rate – Ventura et al., 2004) will arise. Familywise error represents Type I errors (incorrect rejection of a true null hypothesis – false positive) in multiple hypothesis tests and, as more tests are performed, probability of Type I error increases.

To correct the familywise error, a new significance level is defined by using the method developed by Sidak (1967):

$$\alpha_{corrected} = 1 - (1 - \alpha)^{\frac{1}{N}} \quad (2.7)$$

where  $\alpha$  is the significance level or probability ( $\alpha = 0.05$  for Mann-Whitney U tests, 95% probability of a step change);  $\alpha_{corrected}$  is the equivalent significance level that a test should be evaluated at; and  $N$  is the number of repeated tests.

For estimation of the effect size of the Pettitt's test, Common Language Effect Size (CLES) method was used. In the CLES approach, the scores are ranked and all possible data pairs are compared for the compliance with the hypothesis, in our case "the step change". As the name implies, the results are reported in a common language which is the percentage of pairs supporting the step change.

Correction of the family wise error was not implemented in many in many studies that have conducted the Pettitt's test (e.g. Xu et al., 2014). Furthermore, via Sidak correction only the enhanced probability of Type I errors (false positives) are overcome, however the probability of Type II errors (false negatives) should also be considered and again it is lacking in many studies employing the Pettitt test (e.g. Zhang et al., 2014). For estimation of the probability of a false negative ( $\beta$ ), statistical power analysis was performed.

Assuming effect sizes of 0.2, 0.5 and 0.8 with sample from 10 to 50 and assuming ratio of group sizes of 0.5, 0.66 and 0.75, *A priori* power analysis approach was conducted by comparing the asymptotic relative efficiency to a t-test based on Lehman's method. The acceptable power was set at 0.8 (a false negative probability  $\beta = 0.2$ ). According to the power analysis, the probability of a false negative could be approximated as:

$$(1 - \beta) = 0.008T + 0.057d + 0.51\frac{t}{T} - 0.45 \quad r^2 = 0.899, n = 35 \quad (2.8)$$

$$(0.002) \quad (0.06) \quad (0.14) \quad (0.08)$$

where  $T$  is number of years in the time series (up to 39 in this study);  $d$  is the effect size (0.0 to 1.0); and  $t$  is the larger number of years in the time series prior to or after the step change (a maximum of 19 years in this study). The values in brackets below the equation represent the standard errors in the coefficients and the constant term. Also, a significance level of 95% was taken into consideration for inclusion of the variables.

Equation (2.8) shows that for the power analysis of annual records as considered here where the maximum value of  $T$  is 39, then for the statistical power to reach the acceptable threshold of 0.8 (80%), this would only occur for the largest  $T$  (longest time series) where the step change was in the middle of the record ( $\frac{t}{T} = 0.5$ ) and the effect size was large ( $d = 0.9$ ). Therefore, it can be concluded that, although false positives can be eliminated from the Pettitt's test, a high chance of false negatives will still remain.

Pettitt's test was applied to the annual average flux and concentration time series data of Total Reactive Phosphorus (TRP) and Total Phosphorus (TP) for the study period of 1974 - 2012.

## **2.3. Results for Total Reactive Phosphorus**

### **2.3.1. TRP Concentration**

There were 118,547 data that could be paired for concentration and flow from 1974 to 2012 for Total Reactive Phosphorus. The TRP concentration data had a median of 0.145 mg P/l with a 5<sup>th</sup> to 95<sup>th</sup> percentile range of 0.008 to 2.2 mg P/l. Prior to analysis, the Anderson-Darling test was performed and the data was found not to be normally distributed but log transformation was sufficient to normalise the data.

An analysis of variance and covariance on TRP concentration records (Table 2.1) showed that both factors were significant with site factor being the most important factor both with and without the covariate. Inclusion of the log-transformed water yield as a covariate had only a negligible effect on explaining the variance on TRP concentration. *Post hoc* comparisons displayed significant differences between most of the sites. This large variance between sites can be explained with different treatment processes of wastewater treatment plants resulting in different forms/amounts of phosphates in their effluents. Since most of the variance is between catchments, investigating P levels on a national level rather than river basins is found to be more convenient. Because of the largeness of the dataset, the main effects plot for the site factor will not be discussed in this study.

*Table 2.1 Results of ANOVA and ANCOVA on Total Reactive Phosphorus (TRP) Concentration*

Factor or Covariate	Without Covariate		With Covariate	
	P-value	Proportion of variance ( $\omega^2$ )	P-value	Proportion of variance ( $\omega^2$ )
<i>ln(Water Yield)</i>	-	-	0.003	0.015
<i>Site</i>	0	96.57	0	96.52
<i>Year</i>	0	2.93	0	2.95
<i>Error</i>	-	0.005	-	0.52

Main effects plots for TRP concentration with respect to the year factor (Figure 2.2) illustrate an overlapping structure for the two sets of concentration data with and without the covariate which indicates that inclusion of the covariate did not create a significant change in the analysis. The TRP concentration has been declining since its peak year; it has fallen from 0.16 mg/L in 1984 to 0.064 mg/L in 2012.

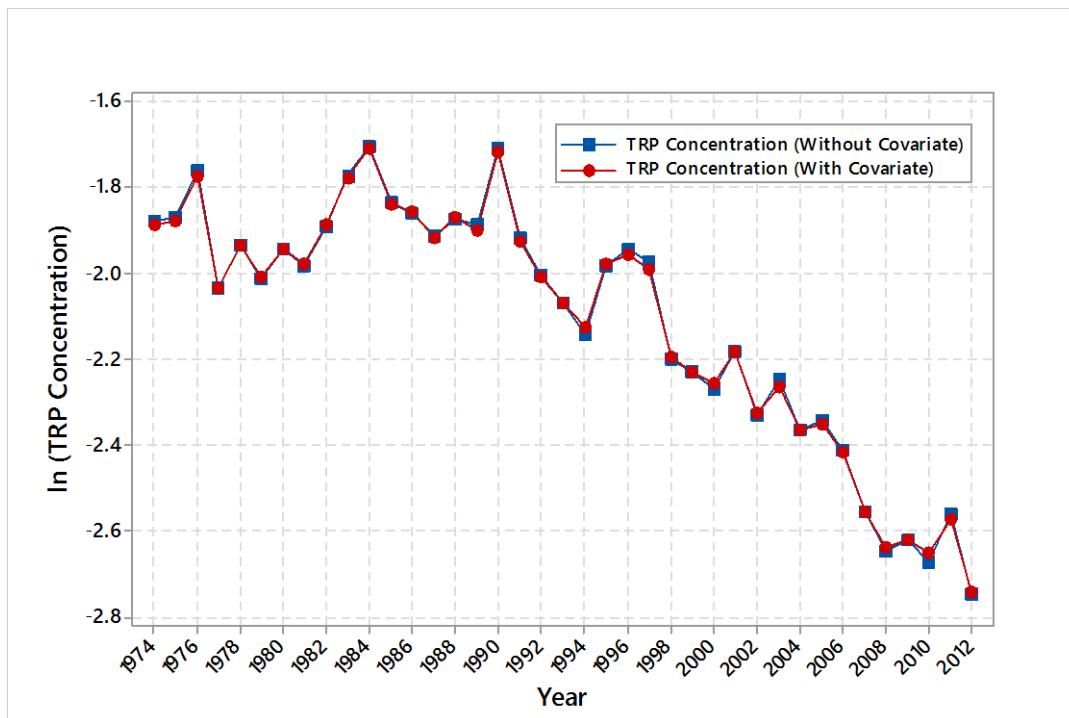


Figure 2.2 Main effects plot for the annual average TRP concentration with and without the covariate over the study period 1974 – 2012.

### 2.3.2. TRP Flux

For the study period of 1974-2012, the number of site-year combinations for which a flux could be calculated for Total Reactive Phosphorus were 4920 and the number of sites for one year's flux can be calculated varied between 16 in 1974 to 167 in 2011. Flux data were also checked for normality via Anderson-Darling test and found not to be normally distributed, and was therefore log-transformed before ANOVA/ANCOVA. All factors were found to be significant at  $p < 0.05$  with the site being the most important factor both with and without the covariate (Table 2.2). When the log-transformed water yield was included as the covariate, it significantly reduced the importance of the site factor. Also, the importance of the year factor was diminished by the inclusion of the covariate.

Table 2.2 Results of ANOVA and ANCOVA on Total Reactive Phosphorus (TRP) Flux

Factor or Covariate	Without Covariate		With Covariate	
	P-value	Proportion of variance ( $\omega^2$ )	P-value	Proportion of variance ( $\omega^2$ )
<i>ln(Water Yield)</i>	-	-	0	9.25
<i>Site</i>	0	96.94	0	88.25
<i>Year</i>	0	2.12	0	1.92
<i>Error</i>	-	0.009	-	0.58

Main effects plot of the year factor with respect to the TRP both with and without the flow covariate display a fluctuating decrease for each component (Figure 2.3). Inclusion of the covariate had a smoothing effect on the main effects of TRP flux by reducing the peak sizes and resulted in a clearer main effects profile for the flux. As for the TRP concentration (Figure 2.2) the TRP flux has been in decline since the mid-1980s confirming that the effect observed in Figure 2.3 is not due to hydroclimatic drivers such as changing river flows but does represent a real decline in the amount of phosphorus moving through the fluvial network..

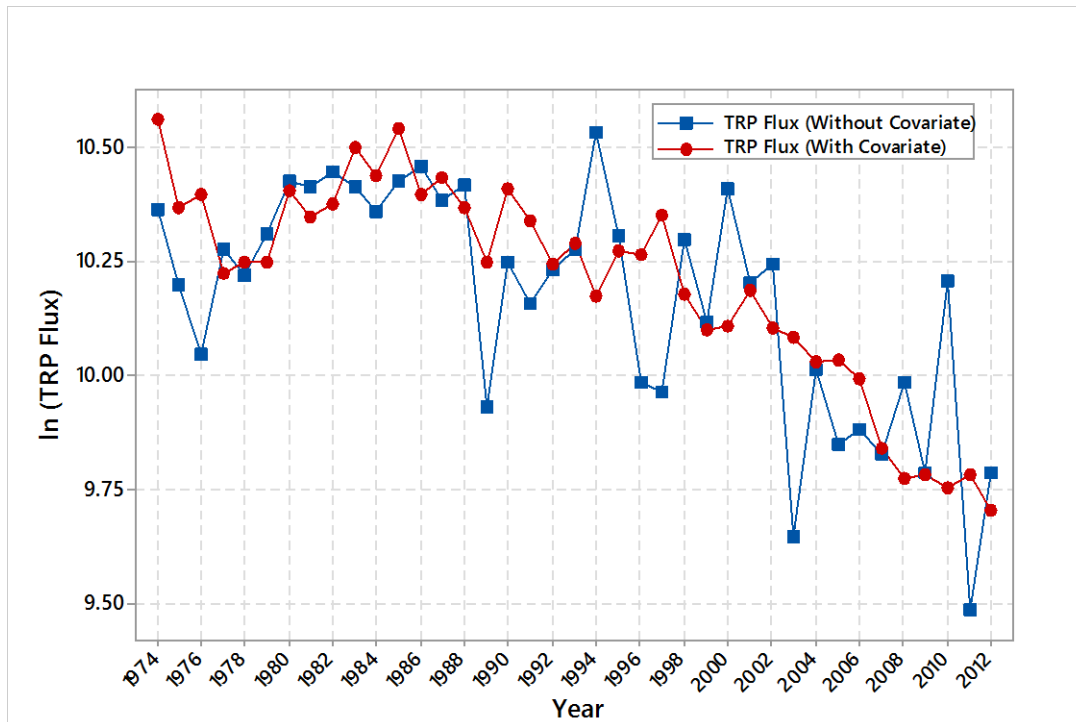


Figure 2.3 Main effects plot for the annual average TRP flux with and without the covariate over the study period 1974 – 2012

The total TRP flux from the UK (Figure 2.4) given by Worrall et al. (submitted), illustrated a decrease in total UK TRP flux since the mid-1980s which is in compliance with the decrease in the main effects plot of TRP flux (Figure 2.3). A sharp decrease was observed in 1993 and also a peak was present in 2002 in the total TRP flux profile. However, such a sharp drop or a high peak was not observed in the main effects.



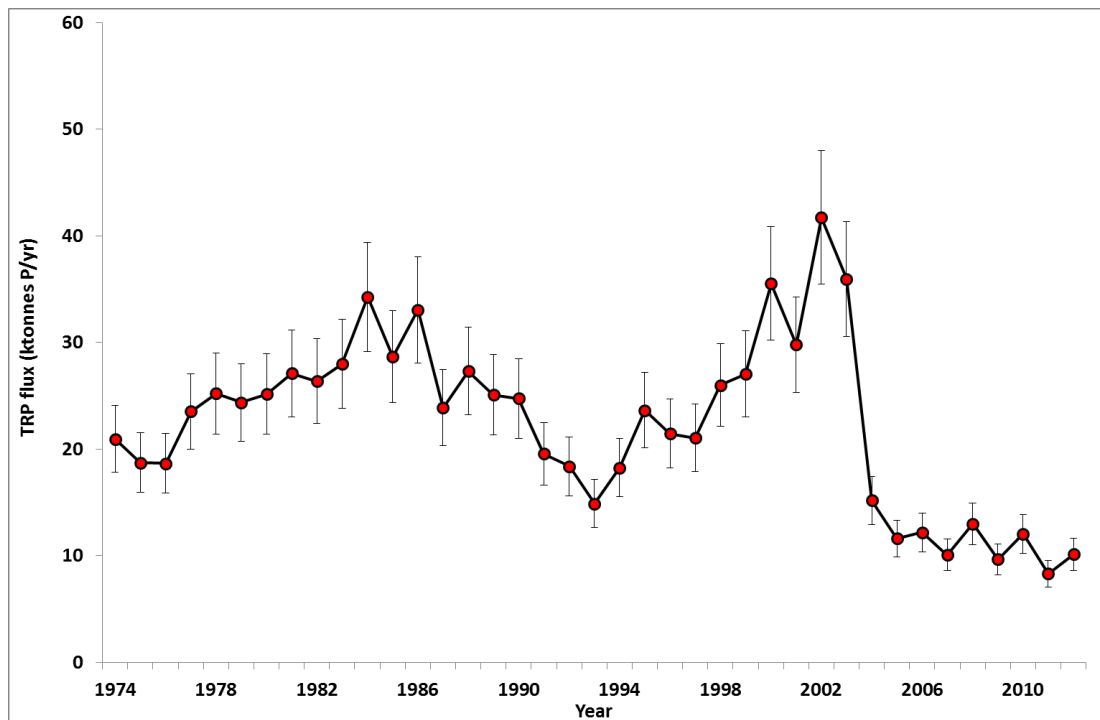


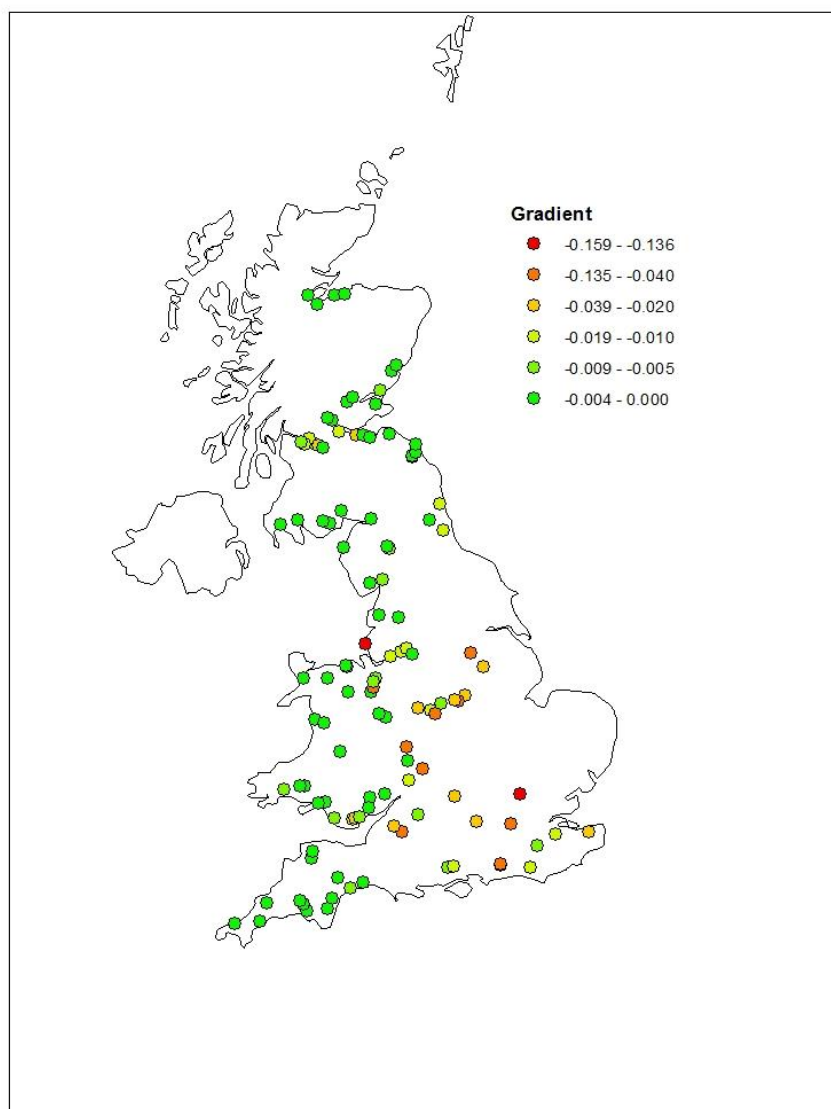
Figure 2.4 TRP flux from the UK over the period 1974 – 2012 (Worrall, *et al.*, submitted)

### 2.3.3. TRP Trend Analysis

#### 2.3.3.1. Overall Trends

Out of 230 sites, there were 143 sites having a length of time series of 20 or more years for TRP concentration and flux. In the concentration time series, 116 sites had negative and 23 sites had positive trends while the remaining 4 sites had no significant trend. Among the 143 sites available for TRP concentration trend analysis, 84 of them are averaging below 0.2 mg/l and 76 sites are averaging below 0.1 mg/l by the end of the study period 1974-2012. Similarly, for the flux time series of TRP, 92 sites showed negative and 41 sites showed positive trends while 9 sites had no significant trends. A spatial distribution map of the sites with negative TRP concentration trends (Figure 2.5) illustrated that the sites with larger declines were

from the Midlands and South East Regions of England whereas South West England, Wales and Scotland has not seen large declines.



*Figure 2.5 Spatial distribution map of the negative TRP concentration trends for the overall study period*

The largest significant decline in the TRP concentration was observed in time series of River Alt above Altmouth pumping station (National Grid Reference

(NGR): SD2921105091) in which the TRP concentration and flux has been declining since 1979 and 1981, respectively and displaying a sharp peak in year 1990 (Figure 2.6).

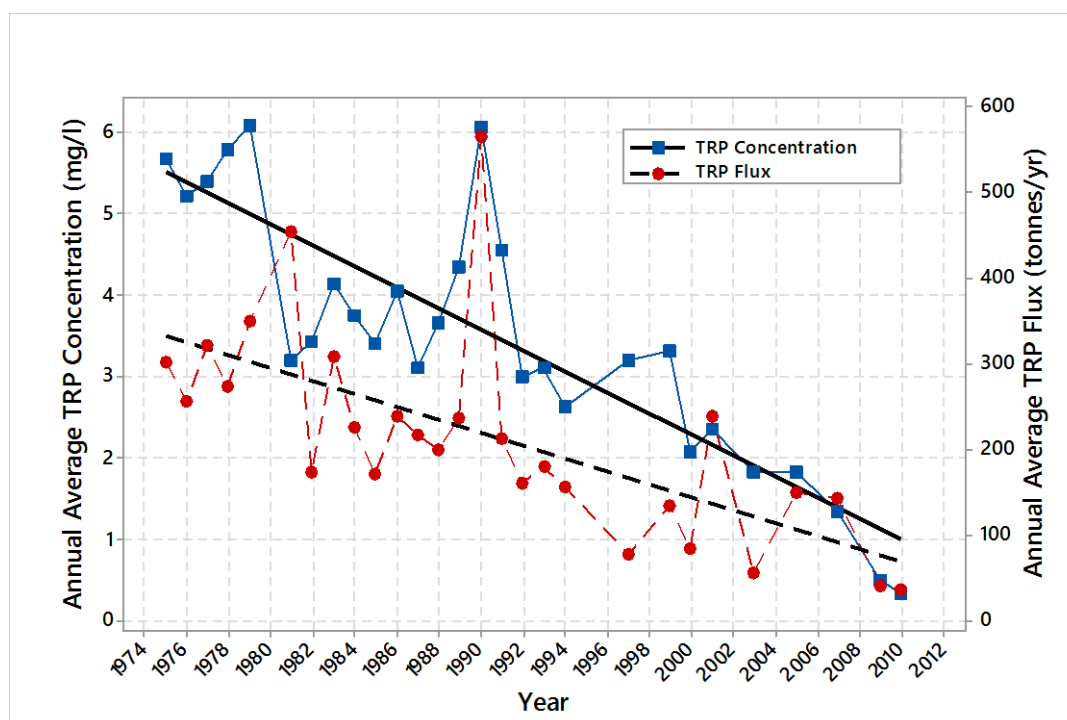


Figure 2.6 TRP concentration and flux time series of River Alt above Altmouth pumping station over the study period 1974 – 2012

The largest significant increase in TRP concentration time series was observed in the records of River Douglas at Wanes Blades Bridge (NGR: SD4758912612) – the annual average TRP concentration and flux time series are shown in Figure 2.7. The TRP concentration records indicate an increase from the start until the year 1996 and both concentration and flux records are peaking in years 2006 and 2005, respectively. There are no records available both for concentration and flux between the years 1997 - 2001, thus it is difficult to explain whether there are any other trends leading to the peak years.

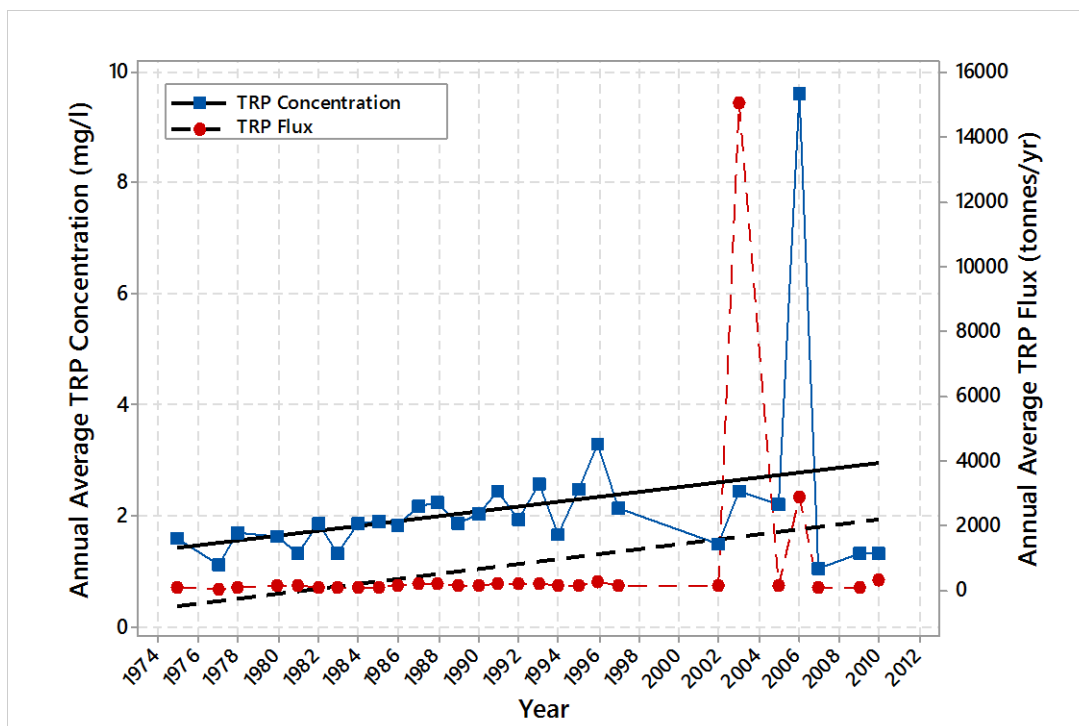


Figure 2.7 TRP concentration and flux time series of River Douglas at Wanes Blades Bridge over the study period 1974 – 2012

Another example of the TRP trends is River Leven at Renton Footbridge (NGR: NS389783); Figure 2.8 illustrates that the annual average TRP concentration and flux time series do not have significant trends despite the peak in year 1992.

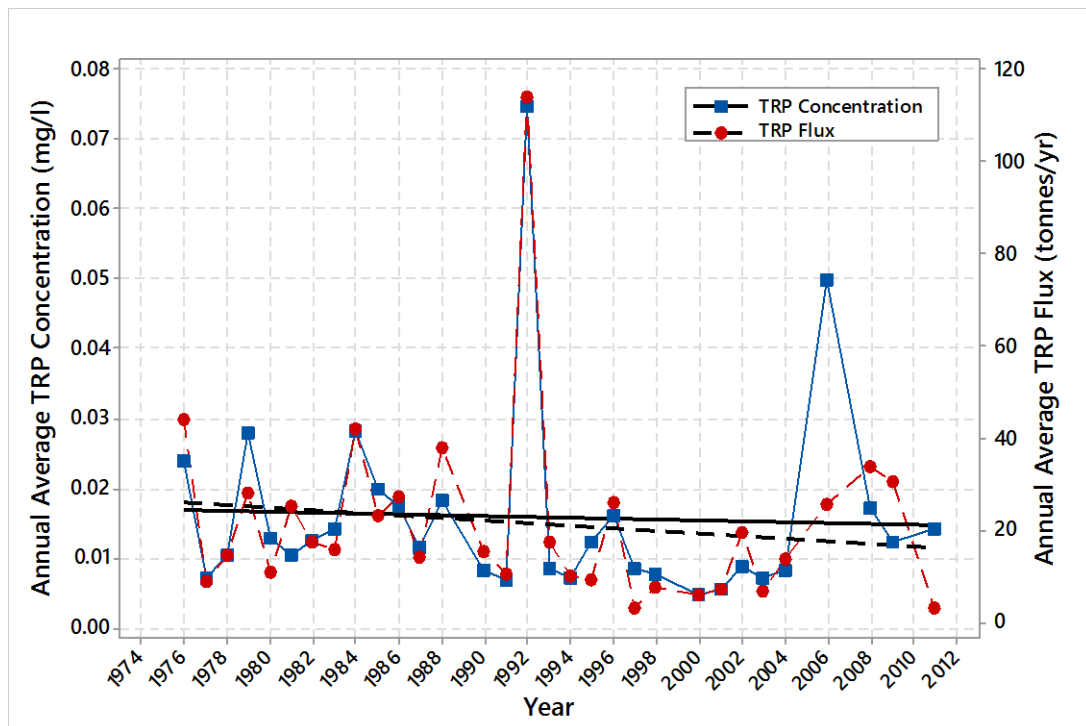
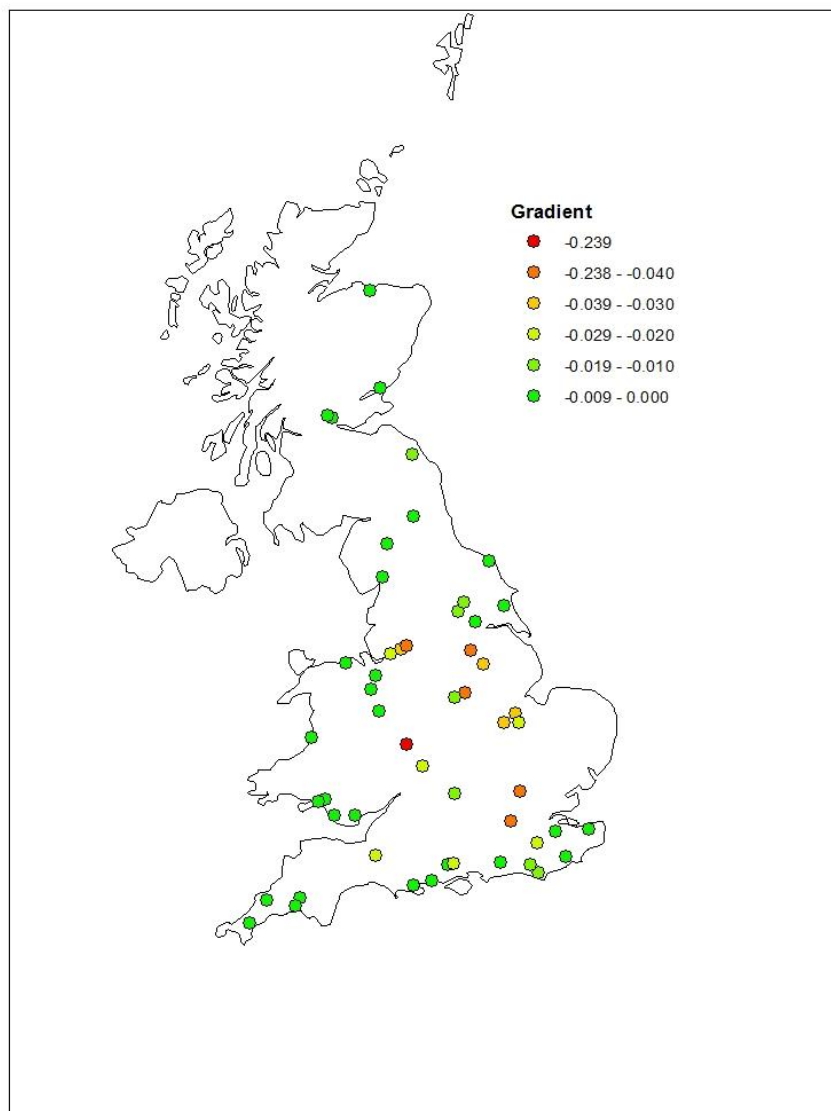


Figure 2.8 TRP concentration and flux time series of River Leven at Renton Footbridge over the study period 1974 – 2012

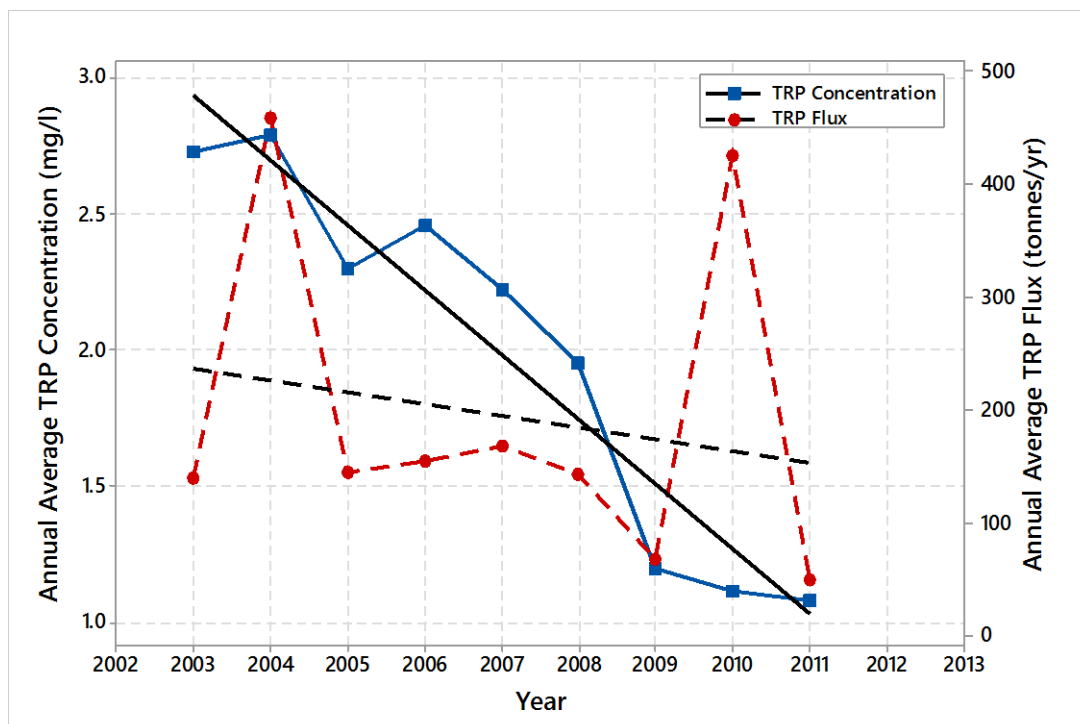
### 2.3.3.2. Trends in the Last Decade

There were 80 sites having 8 or more years of TRP concentration and flux data between years 2003-2012 – the last decade of the study period. For the concentration time series, 54 sites had negative trends, 22 sites had positive trends and the remaining 4 sites had no significant trend. By the end of the decade all the sites had an average below 0.2 mg/l and 79 sites had an average below 0.1 mg/l for TRP concentration. The spatial distribution map for the negative TRP concentration trends in the last decade of the study period (Figure 2.9) indicated that the sites with larger declines were from the Midlands and South East regions of England.



*Figure 1.9 Spatial distribution map of the negative TRP concentration trends for the last decade of the study period*

Figure 2.10 shows the annual average TRP concentration and flux time series for the River Stour at Stourport Footbridge (NGR: SO8127070790); the site with the sharpest decline in TRP concentration time series in the last decade of the study period.



*Figure 2.10 TRP concentration and flux time series of River Stour at Stourport Footbridge over the last decade of the study period.*

The site with the largest increase in TRP concentration time series in the last decade of the study period was River Alyn at Ithels Bridge (NGR: SJ3902056230) (Figure 2.11)

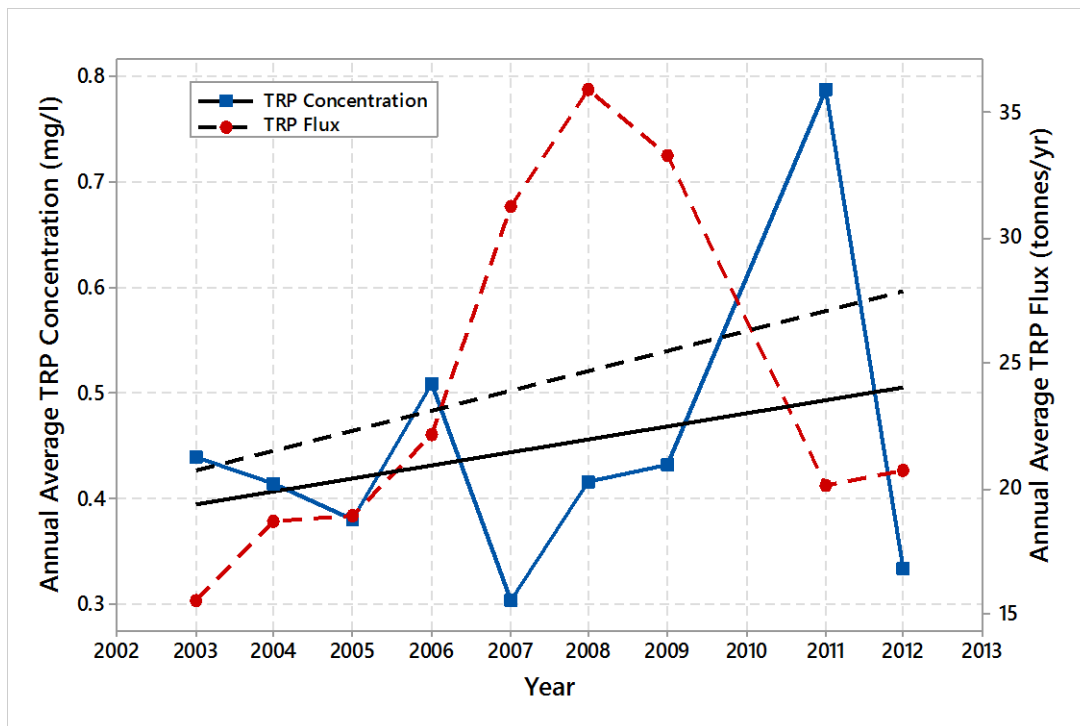


Figure 2.11 TRP concentration and flux time series of River Alyn at Ithels Bridge over the last decade of the study period

Another example of the last decade trends is River Tawe at Morrision Road Bridge (NGR: SS6736797989) with no trend in its annual average TRP concentration time series (Figure 2.12). Although, there is no trend in concentration, flux of TRP is increasing possible due to increased flow.



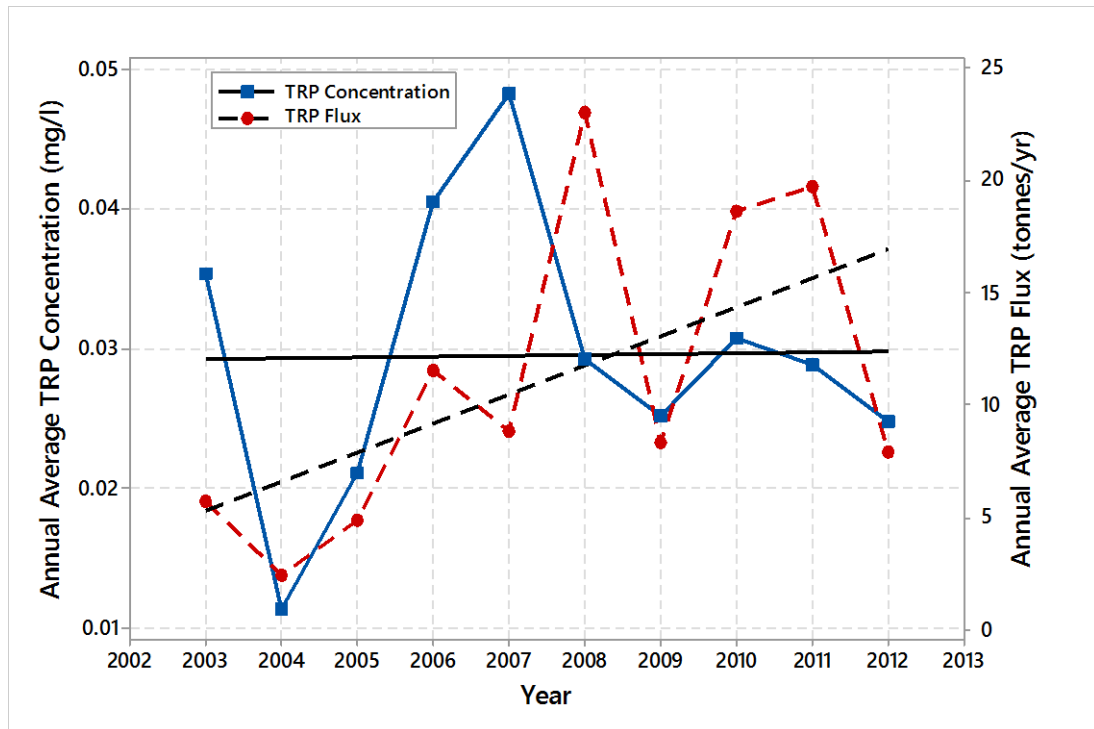
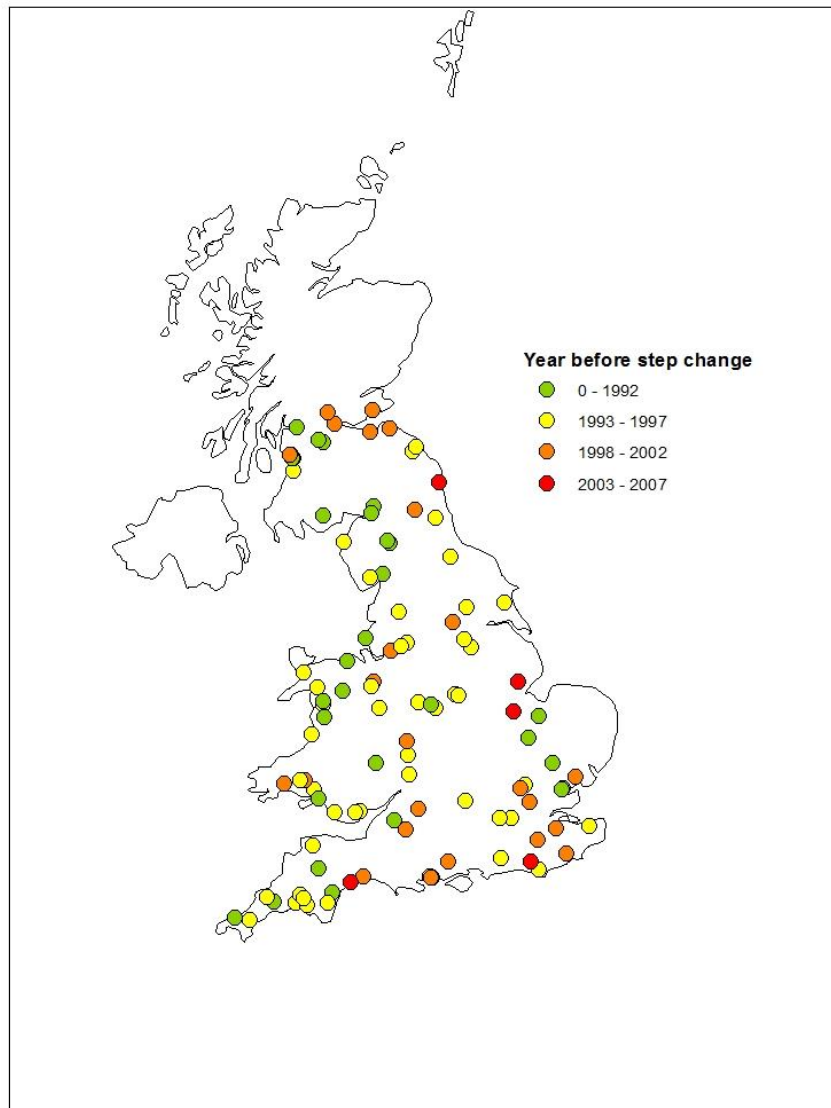


Figure 2.12 TRP concentration and flux time series of River Tawe at Morrision Road Bridge over the last decade of the study period

#### 2.3.4. Change Point Analysis

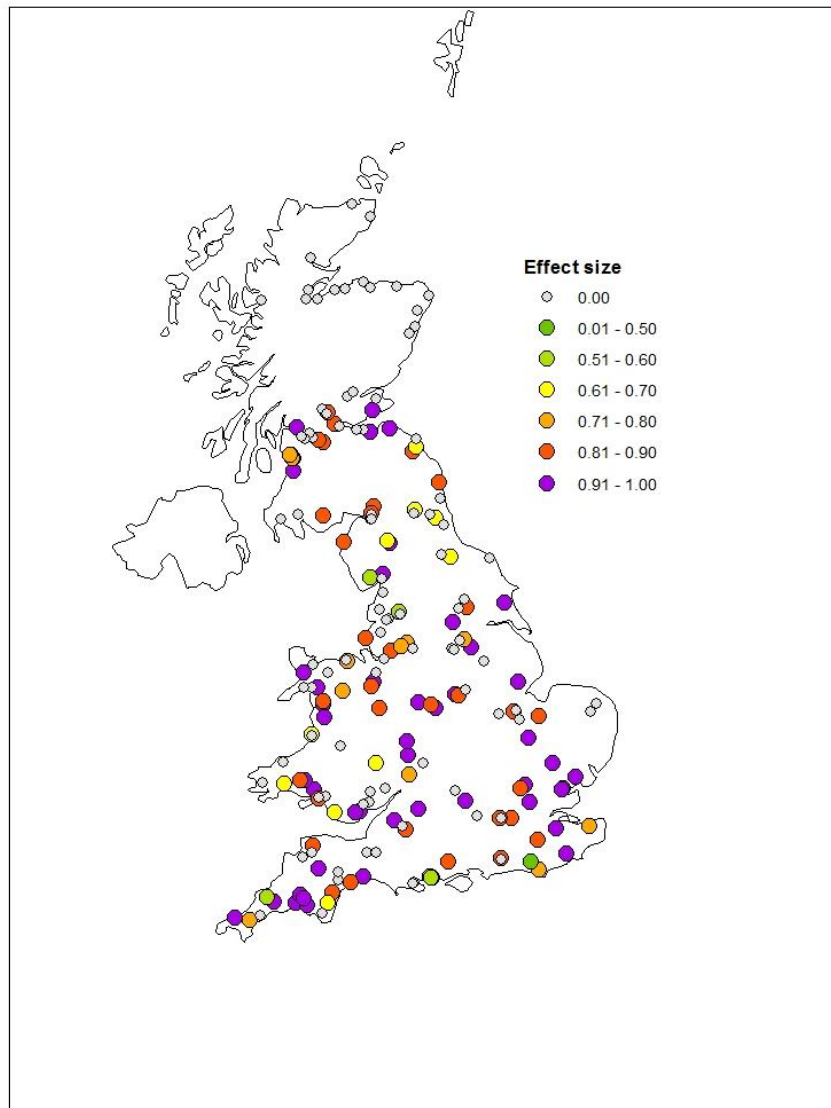
For the annual average concentration of TRP of the 230 sites where a record could be tested, 136 sites for TRP showed a significant step change after family wise correction; all the significant step changes were a step decline to a lower annual average. Figure 2.13 illustrates the spatial distribution map of TRP concentration step changes in the UK (except Northern Ireland) with respect to different time periods. According to the map, most of the step changes occurred in years between 1993 – 1997, and very few step changes were detected in the period of 2003 – 2007.



*Figure 2.13 Spatial distribution map of TRP concentration step change year intervals in the Great Britain*

Common language effect sizes of the steps in TRP concentration varied in the range of 0.14 - 1.00 with a geometric mean of 0.89. Figure 2.14 displays the spatial distribution map of effect sizes of TRP concentration in the UK. It can be inferred from the map that most of the effect sizes of steps were large – in the ranges between 0.91 – 1.00 and 0.81 - 0.90. In addition to CLES, actual sizes of the step changes

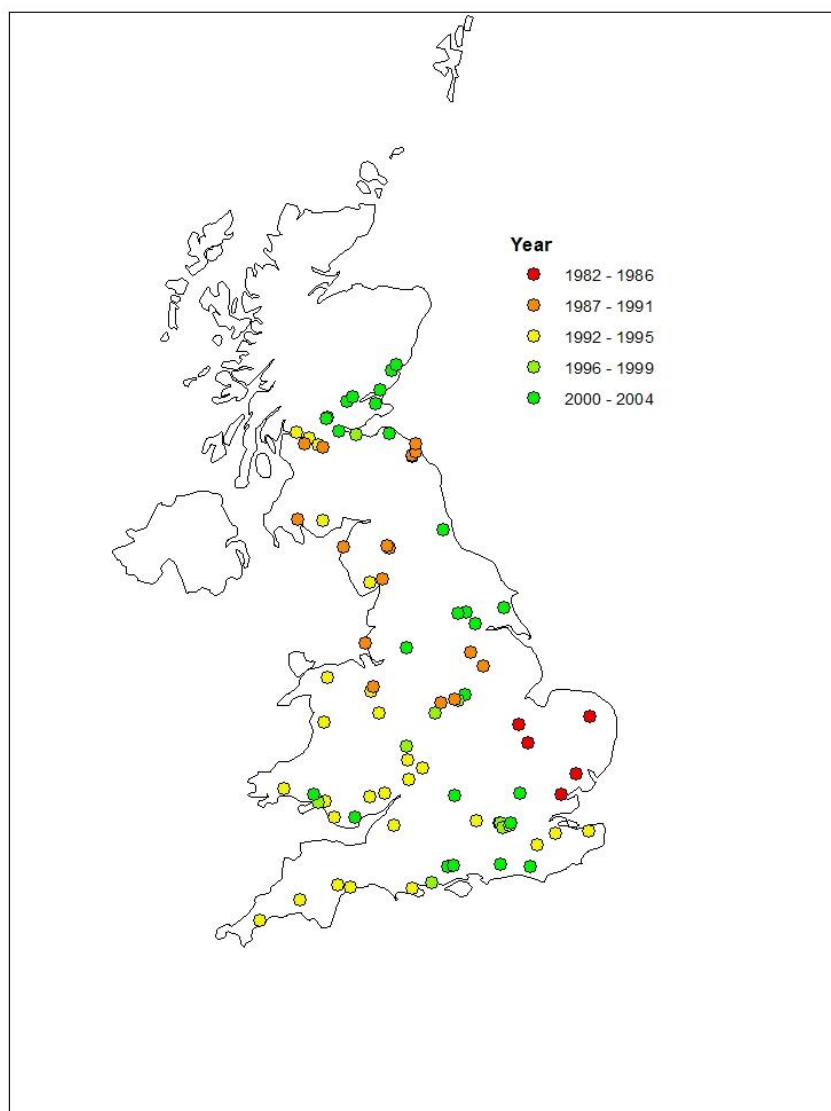
were calculated by using the average concentrations before and after the year of step. For TRP concentration, the actual sizes to the step changes were in the range 96% – 6.7% with geometric mean of 49% (magnitudes of changes were in the range between 0.001 mg/l and 2.36 mg/l with a geometric mean of 0.13 mg/l). Figure 2.11 and Figure 2.12 show that step changes were rare for the rivers in Northern Scotland – an area of low population; extensive upland and livestock farming.



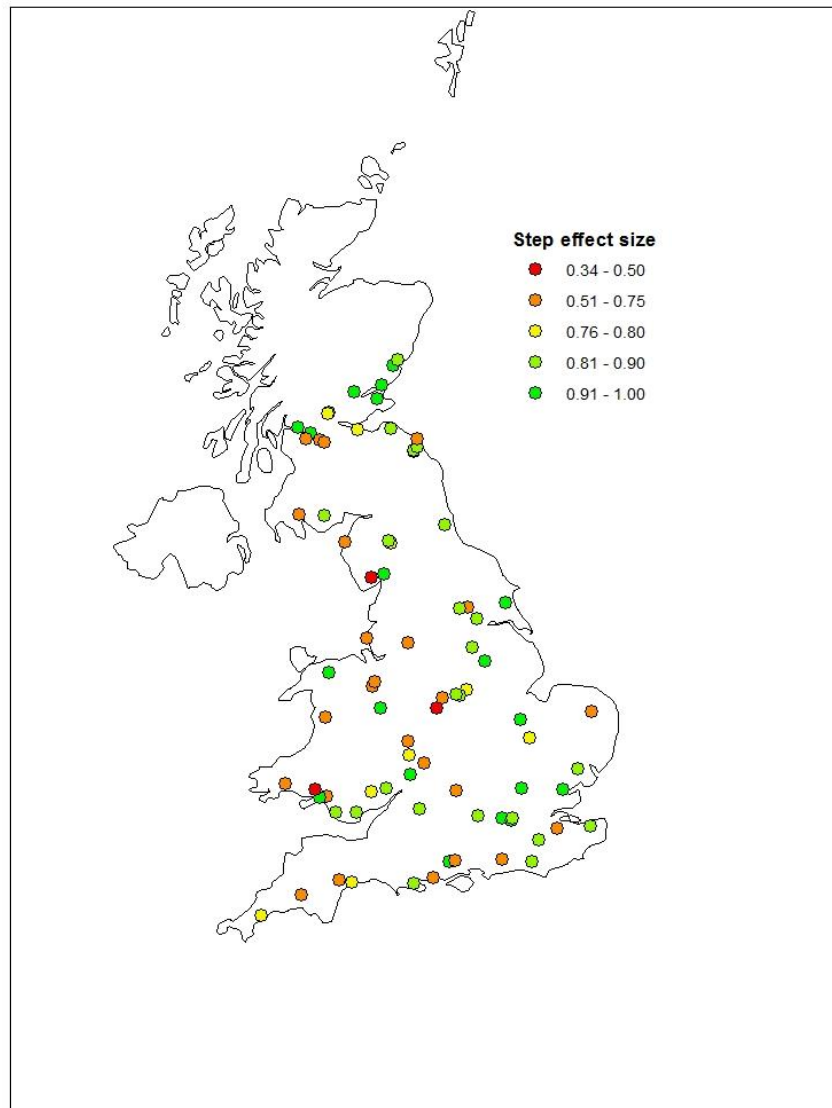
*Figure 2.14 Spatial distribution map of TRP concentration effect size intervals of the step changes in the Great Britain*

For the annual average TRP flux records, the number of sites having a significant step change were lower than the ones in annual average TRP records. After familywise correction, 74 sites for TRP flux were found to have step changes with common language effect sizes in the range 0.46 - 0.99 and geometric mean of 0.87. The actual size of the step changes in flux were calculated to be in the range

97% – 5.8% with geometric mean of 50% for TRP (magnitudes of changes were in the range between 0.33 ktonnes/yr and 1702 ktonnes/yr with a geometric mean of 38.9 ktonnes/yr). Spatial distribution map for the TRP flux step change years (Figure 2.15) indicated that most of the step changes were in the periods 1992 - 1995 and 1996 – 1999. Given that and most of the concentration step changes also occurring in a similar period of 1993 – 1997 (seen in Figure 2.13), it can be inferred that the real source of change is concentration and not river flow.



*Figure 2.15 Spatial distribution map of TRP flux step change year intervals in the Great Britain*



*Figure 2.16 Spatial distribution map of TRP flux effect size intervals of the step changes in the Great Britain*

## **2.4. Total Phosphorus**

### **2.4.1. TP Concentration**

The number of data that could be paired for TP concentration and flow was 40,887, in the study period of 1974 - 2012. TP concentration had a median of 0.11

mg P/l with a 5<sup>th</sup> to 95<sup>th</sup> percentile range of 0.012 to 1.36 mg P/l. The Anderson-Darling test showed that the data distribution was not normal, and therefore the data were log-transformed.

The ANOVA results (Table 2.3) showed that both factors were significant with site factor being the most important factor for the TP concentration both with and without the covariate. Inclusion of the log-transformed water yield as the covariate increased the importance of the year factor and decreased the proportion of variance explained by the site factor.

*Table 2.3 Results of ANOVA and ANCOVA on Total Phosphorus (TP) Concentration*

Factor or Covariate	Without Covariate		With Covariate	
	P-value	Proportion of variance ( $\omega^2$ )	P-value	Proportion of variance ( $\omega^2$ )
<i>ln(Water Yield)</i>	-	-	0.135	0.006
<i>Site</i>	0	95.38	0	95.21
<i>Year</i>	0	3.35	0	3.43
<i>Error</i>	-	1.27	-	1.35

Main effects plot of TP concentration with respect to the year factor with and without the covariate (Figure 2.17) displays an overlapping structure indicating that the inclusion of the covariate did not have a very large effect on ANOVA. The TP concentration peaked in 1985 and has been declining since that year; the concentration has fallen from 0.33 mg/L in 1985 to 0.10 mg/L in 2012. Main effects plot of TP concentration does show a sharp decrease in 1994, the only possible



reason for this is a change in sampling in that year, however it should be pointed out that by using ANOVA including site and year factors the time series of the least square means over time should be independent of the site factor. Still the monitoring programme is not completely cross-classified with respect to sites and years of sampling, equally differences between the years might be caused by specific events occurred in particular sites in some years. Therefore, further investigation is necessary via individual analysis of the sites.

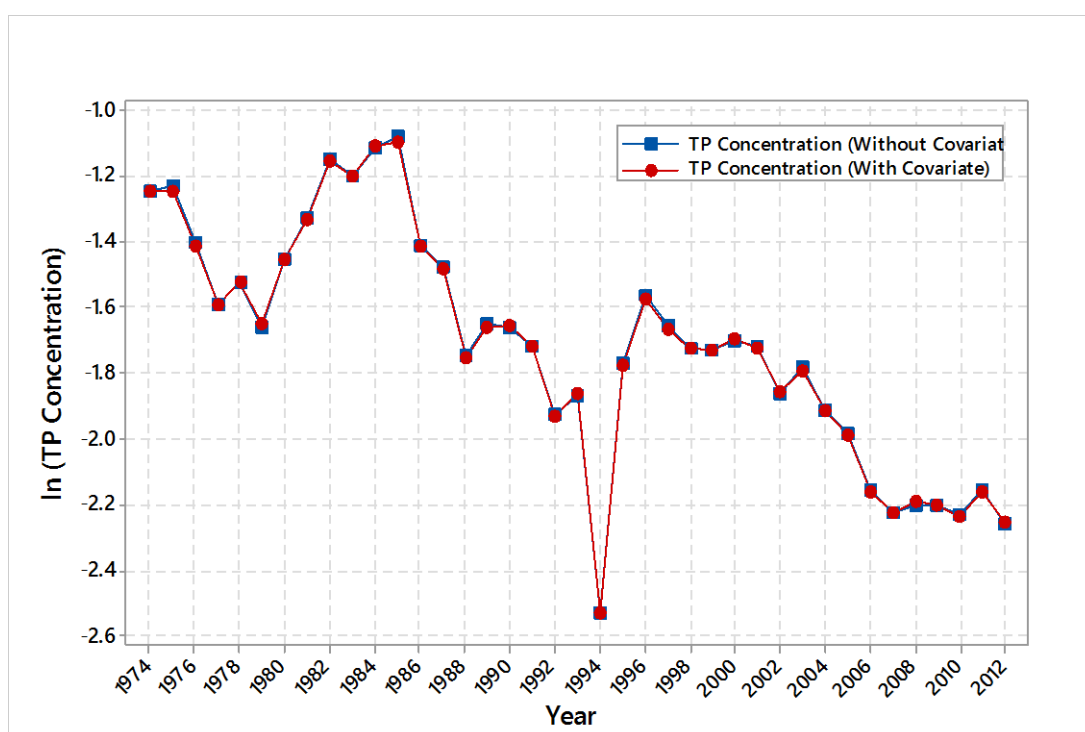


Figure 2.17 Main effects plot for the annual average TP concentration with and without the covariate over the study period 1974 – 2012

## 2.4.2. TP Flux

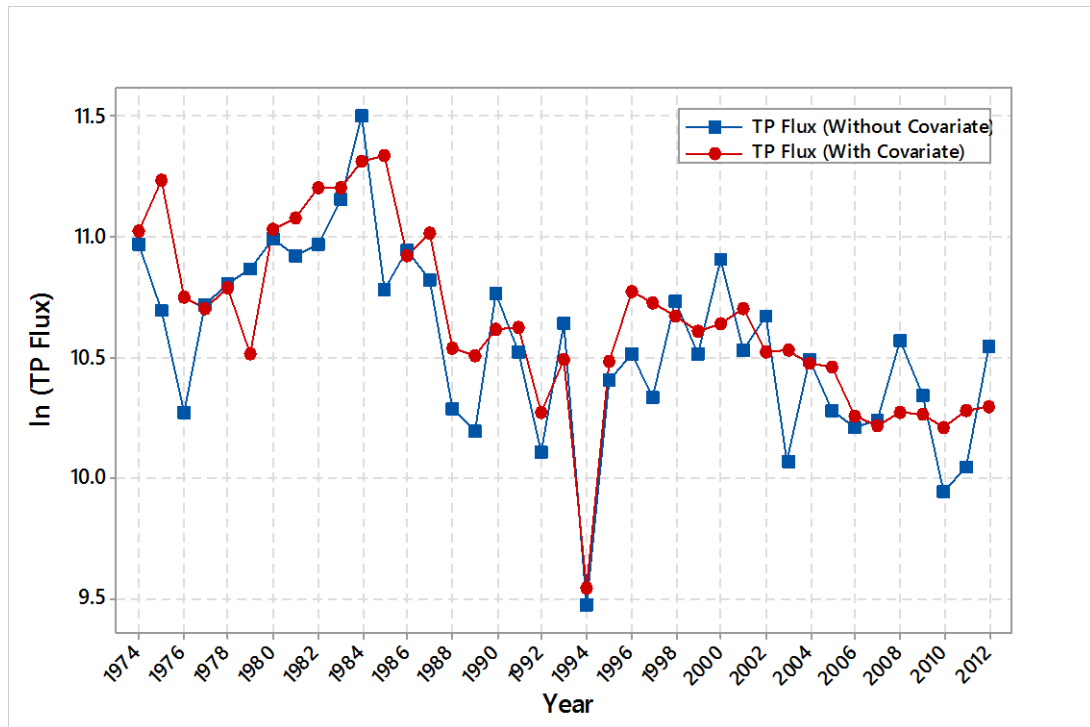
The number of site-year combinations for which a flux could be calculated for TP was 2228 and the number of sites for one year's flux can be calculated for TP was between 1 in 1983 and 199 in 2012. TP Flux data were also checked for normality via Anderson-Darling test and found to have a non-normal distribution: it was therefore log-transformed before ANOVA/ANCOVA.

Analysis of variance (Table 2.4) indicated that both factors were significant at  $p < 0.05$  with the site being the most important factor both with and without the covariate. When the water yield was included in the analysis as the covariate, importance of both site and year factors diminished.

Table 2.4 Results of ANOVA and ANCOVA on Total Phosphorus (TP) Flux

Factor or Covariate	Without Covariate		With Covariate	
	P-value	Proportion of variance ( $\omega^2$ )	P-value	Proportion of variance ( $\omega^2$ )
<i>ln(Water Yield)</i>	-	-	0	16.16
<i>Site</i>	0	94.01	0	79.44
<i>Year</i>	0	2.94	0	2.70
<i>Error</i>	-	3.04	-	1.69

Main effects plot of the year factor with respect to the TP flux both with and without the flow covariate (Figure 2.18) displays a fluctuating profile with flux decreasing since the mid-1980s. As with the main effect plot of concentration over time (Figure 2.17) there is a sharp decrease in the least squares mean for TP flux in 1994.



*Figure 2.18 Main effects plot for the annual average TP flux with and without the covariate over the study period 1974 – 2012*

The total TP flux from the UK (Figure 2.19) given by Worrall et al. (submitted), illustrates a decrease in the TP flux until the year 1994 followed by a slow increase afterwards. The main effects plot of TP flux (Figure 2.18) also shows a decrease until 1994, however such a sharp decrease is not present in the total TP flux profile (Figure 2.19). Also, there are many peaks present in the total TP flux profile (Figure 2.19) that makes it seem like a completely different profile than the main effects (Figure 2.18), and therefore it is hard to correlate the two profiles and make an explanation for the difference.

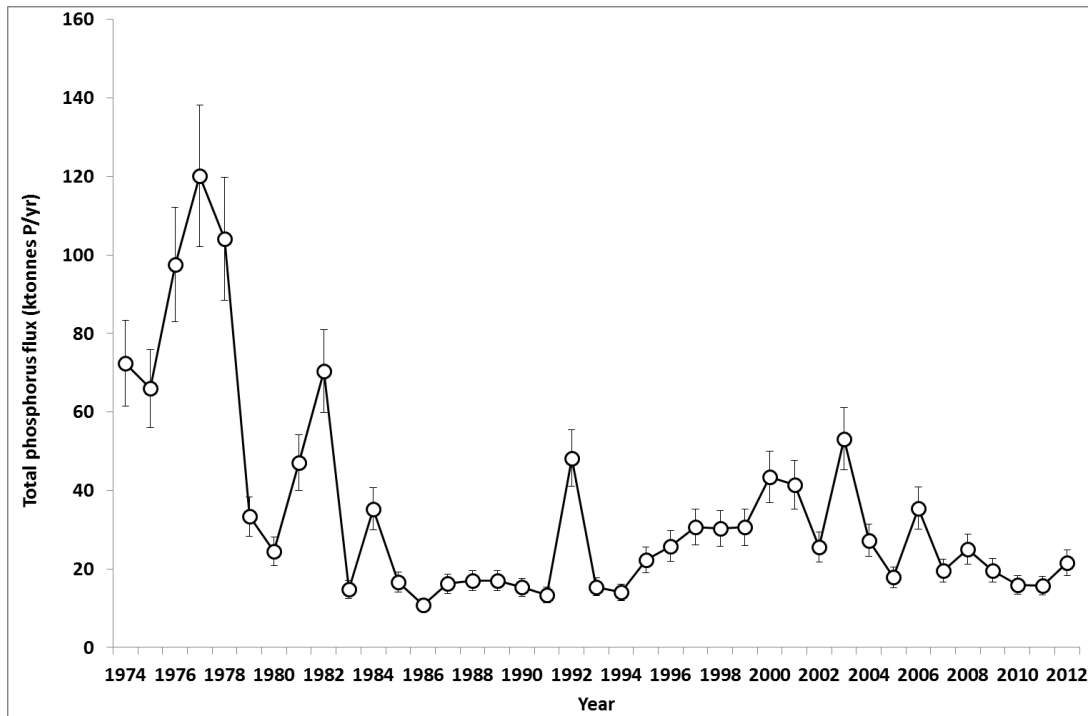


Figure 2.19 TP flux from the UK over the period 1974 – 2012 (Worrall, et al., submitted)

## 2.4.3. TP Trend Analysis

### 2.4.3.1. Overall Trends

For TP concentration and flux time series, there were only 8 sites having at least 20 years data for trend analysis. TP concentrations declined to below 0.2 mg/l in 6 of the sites and below 0.2 mg/l in 5 sites. All the sites showed significant negative trends in both concentration and flux except for one site; River Ness at Inverness (NGR: NH665445). Time series for River Ness (Figure 2.20) shows that both concentration and flux data of TP increased between the years 1994 - 2004 and they have been declining since the peak year.

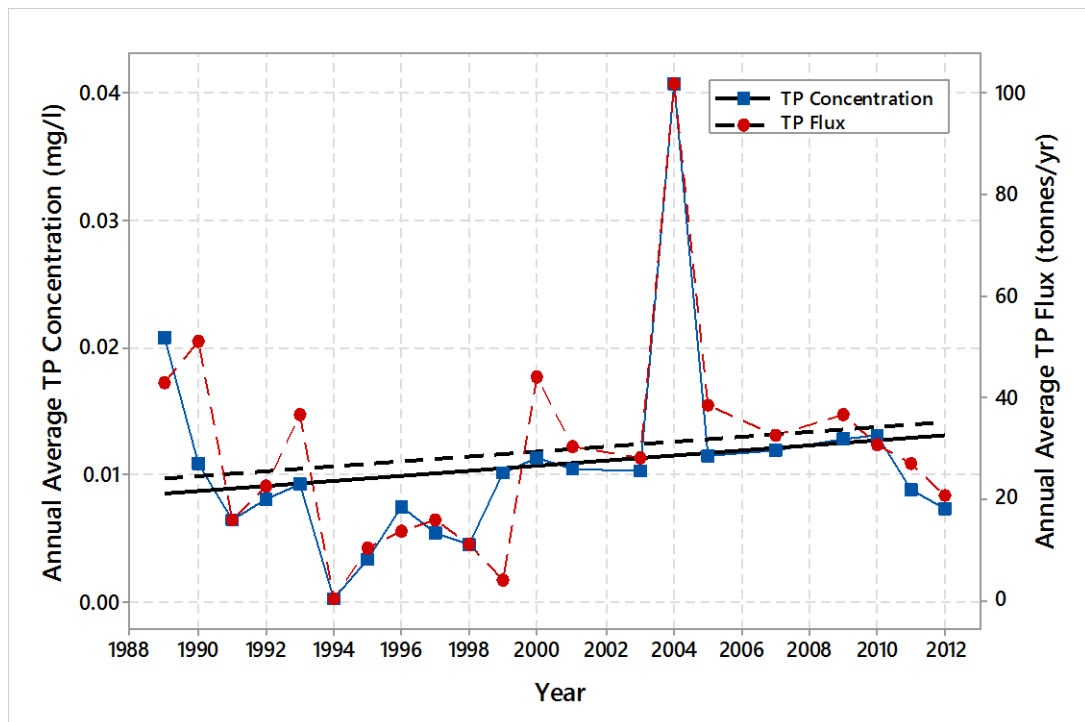
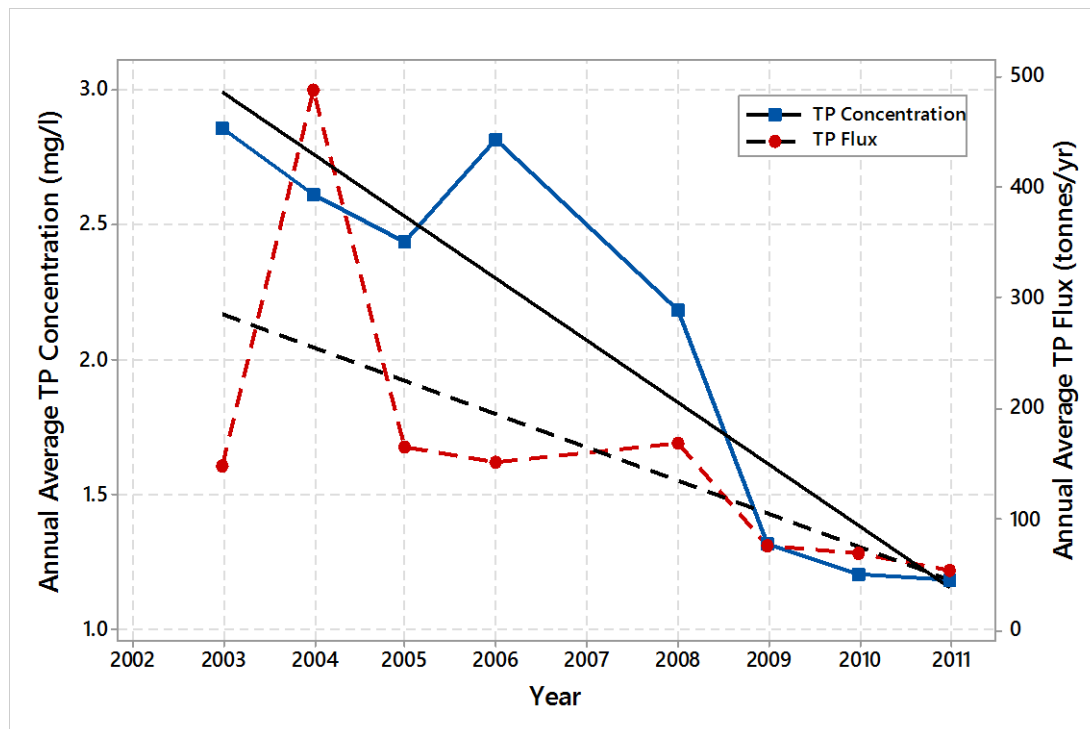


Figure 2.20 TP concentration and flux time series of River Ness at Inverness over the study period 1974 – 2012

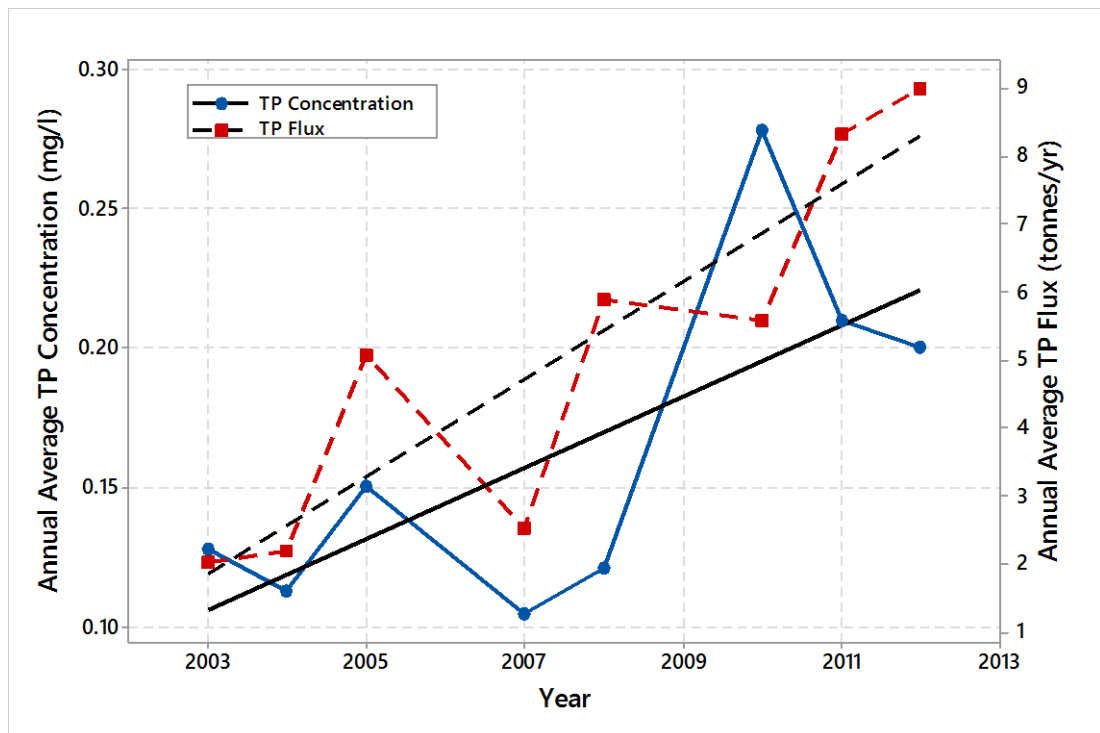
#### 2.4.3.2. Trends in the Last Decade

In the last decade of the study period, 95 sites had 8 or more years of TP concentration and flux data. For concentration time series, 13 sites showed positive trends, 78 sites showed negative trends and 3 sites did not show any significant trend. Among these sites, 93 of the sites declined to have an averaging below both 0.2 mg/l and 0.1 mg/l for TP concentration. For the flux time series, 47 sites had positive trends, 44 had negative trends whereas 3 sites had no significant trend. The site with the steepest decline in TP concentration and flux time series is River Stour at Stourport Footbridge (NGR: SO8127070790) (Figure 2.21).



*Figure 2.21 TP concentration and flux time series of River Stour at Stourport Footbridge over the last decade of the study period*

River Carnon at Devoran Bridge (NGR: SW7908739436) had the largest increase in TP concentration and flux time series in the last decade of the study period (Figure 2.22).



*Figure 2.22 TP concentration and flux time series of River Carnon at Devoran Bridge over the last decade of the study period*

Another example is River Mawddach at Ganllwyd (NGR: SH7297023370) with no significant trend in TP concentration time series (Figure 2.23)

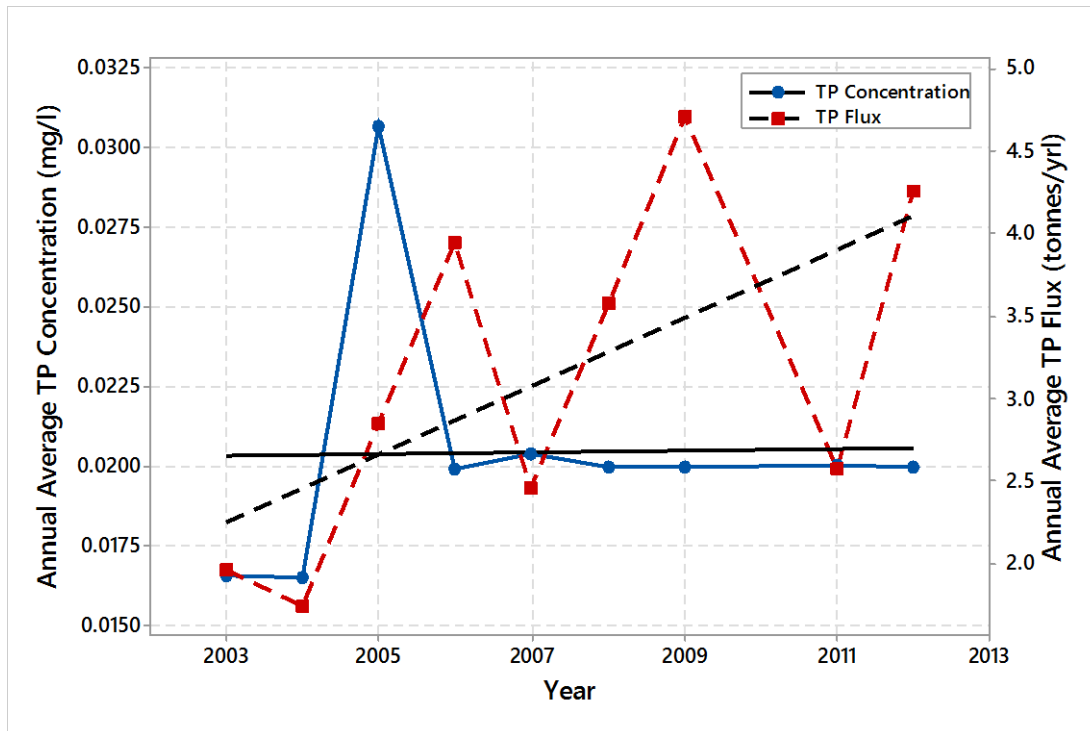


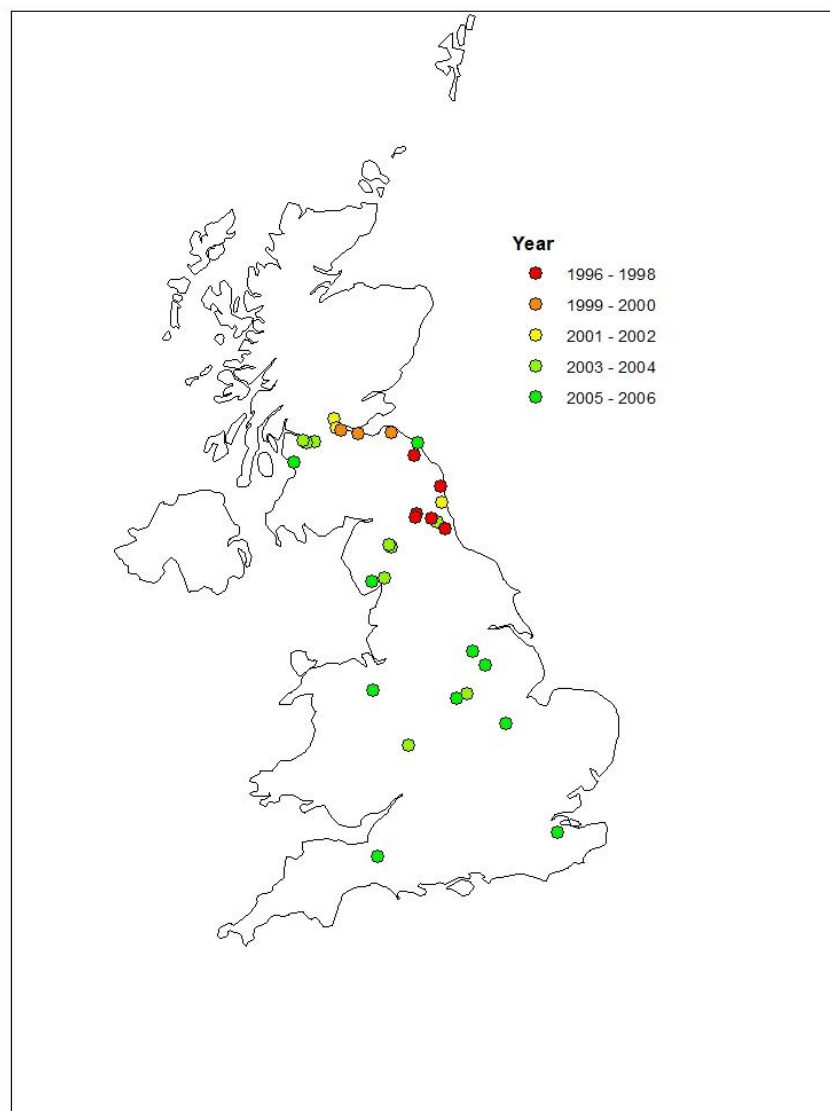
Figure 2.23 TP concentration and flux time series of River Mawddach at Ganllwyd over the last decade of the study period

#### 2.4.4. Change Point Analysis

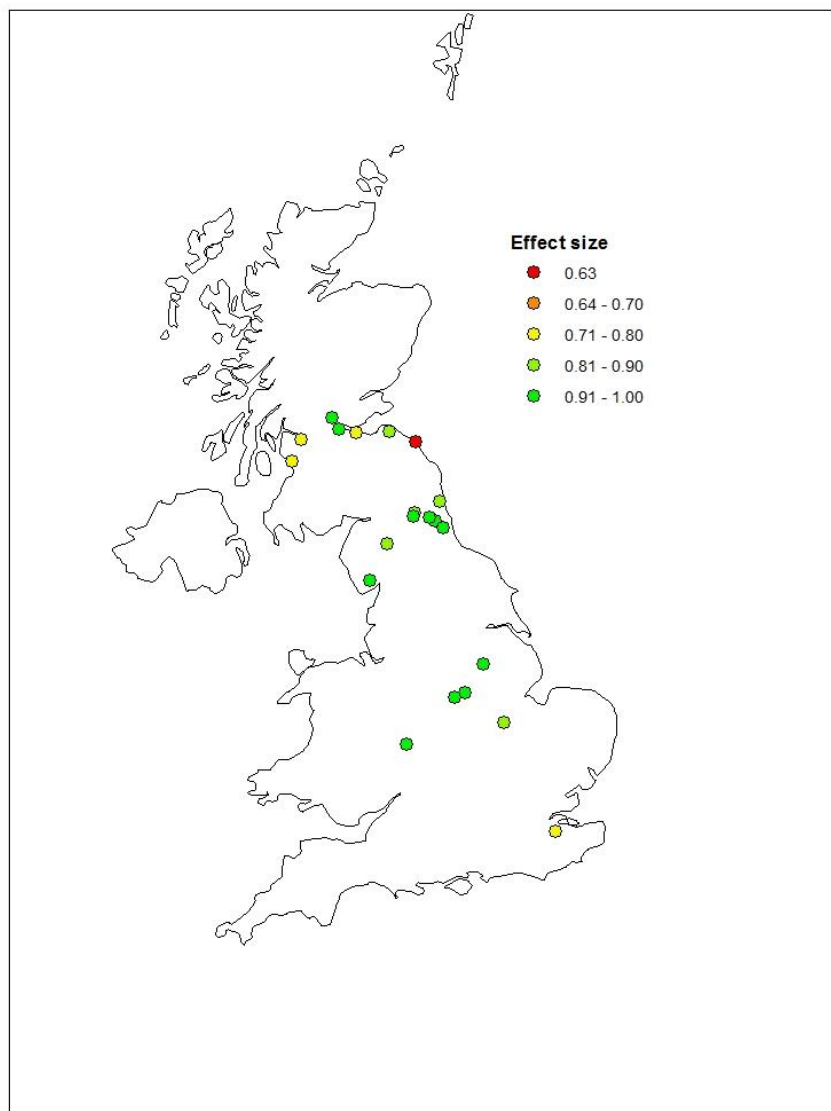
For the annual average TP concentration, 31 sites were found to have significant step changes (after familywise correction) with all the step changes being to lower concentrations with common language effect sizes in the range of 0.80 - 1 with a geometric mean of 0.93. Also, the actual sizes to the step changes were estimated to be in the range of 83% – 20% with geometric mean 50% for TP concentration (magnitudes of changes were in the range between 0.013 mg/l and 1.72 mg/l with a geometric mean of 0.16 mg/l). Spatial distributions map for TP concentration step changes in Figures 2.24 and 2.25 illustrated that most of the



changes were in the period of 2003 – 2006. This is because of the scarcity of the TP records; most of the sites had very few data before the last decade of the study period.

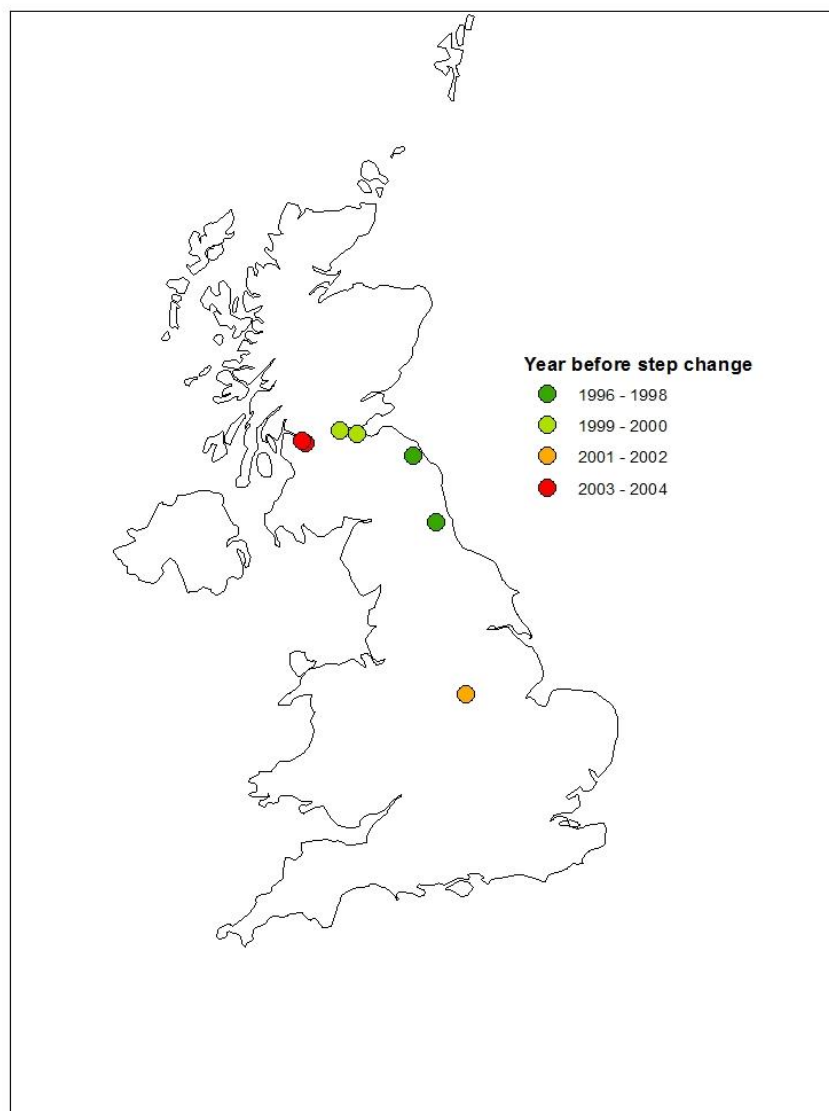


*Figure 2.24 Spatial distribution map of TP concentration step change year intervals in the Great Britain*



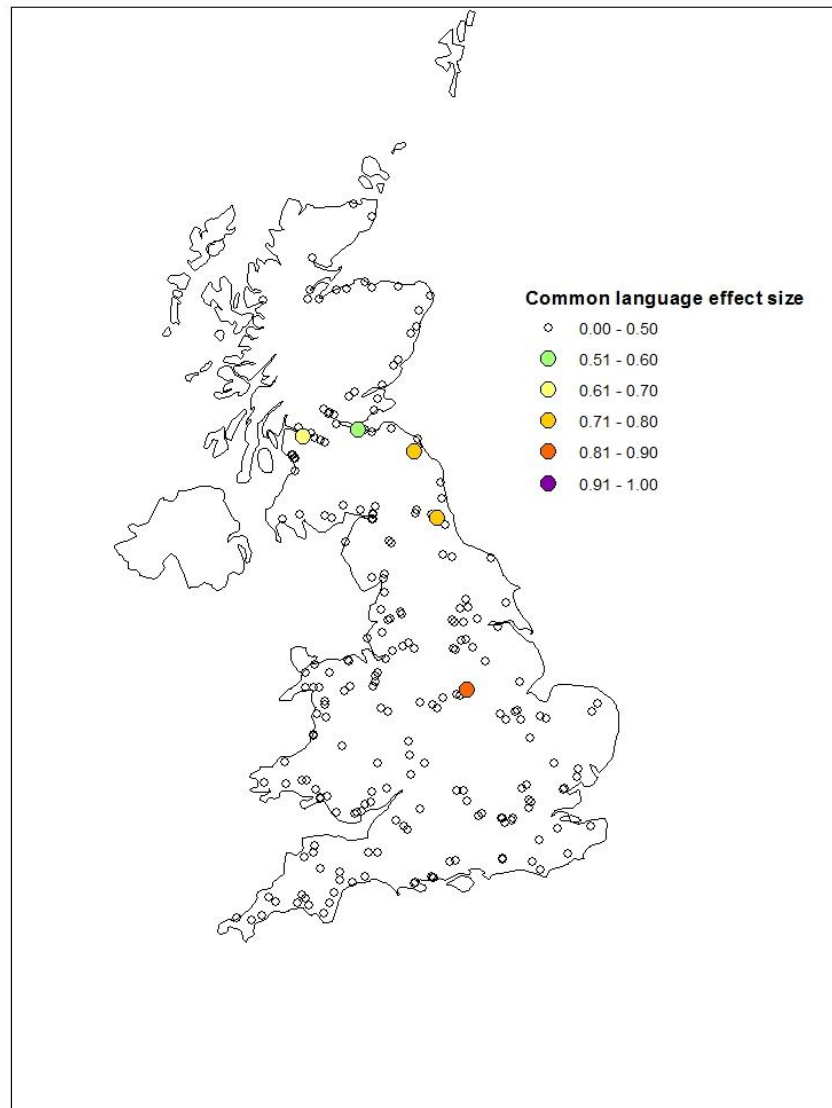
*Figure 2.25 Spatial distribution map of TP concentration effect size intervals of the step changes in the Great Britain*

For the annual average flux records, the number of sites having a significant step change are again lower than the ones in annual TP concentration records. After familywise error correction only 4 sites had statistically significant step changes and these sites are displayed in spatial distribution map below (Figure 2.26).



*Figure 2.26 Spatial distribution map of TP flux step change year intervals in the Great Britain*

The TP flux step changes had common language effect sizes in the range of 0.55 - 0.96 with a geometric mean of 0.79. Spatial distribution map of the effect sizes is given in Figure 2.27. The actual size of the step changes in flux were calculated to be in the range 81% – 32% with geometric mean of 50% for TP (magnitudes of changes were in the range between 9.2 tonnes/yr and 906 tonnes/yr with a geometric mean of 52.6 tonnes/yr).



*Figure 2.27 Spatial distribution map of TP flux effect size intervals of the step changes in the Great Britain*

Figure 2.28 illustrated that for none of the time series considered was there a step change before 1982. For TRP concentration, the modal year of any step change was 1997 but for the TRP flux the modal year was delayed 'til 2000. For TP concentration and flux there was no step change before 1996 add the modal years were 2005 and 2004 respectively.

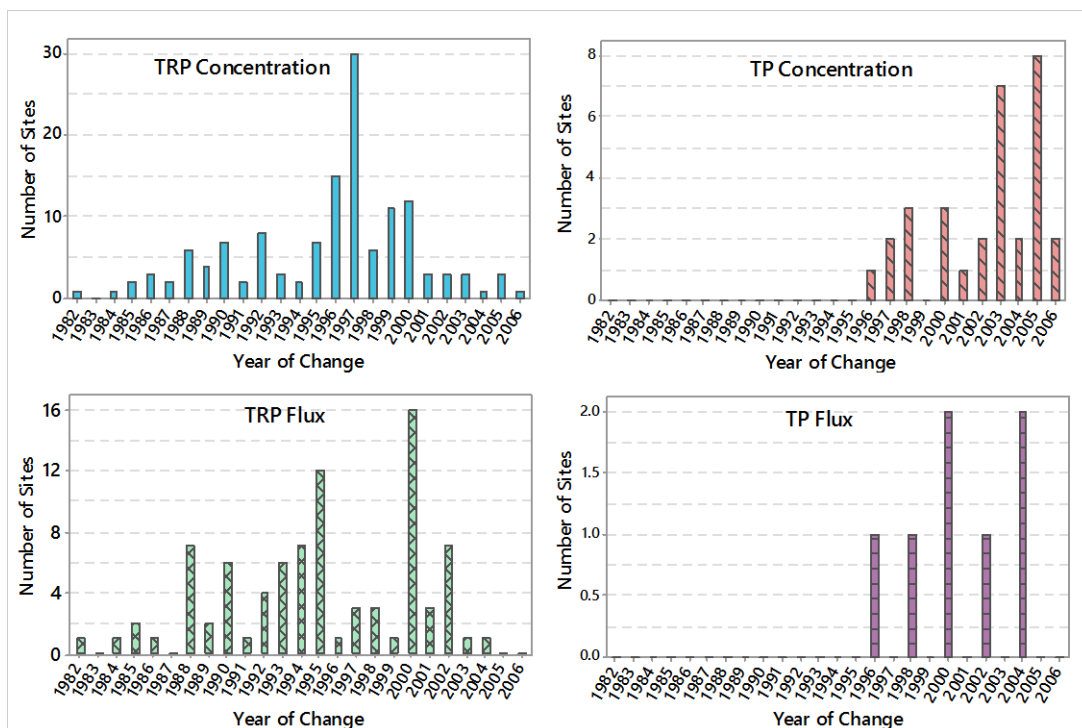


Figure 2.28 Comparisons between step change years in TRP and TP concentration and flux times series records

## 2.5. Discussion

In this chapter, TRP and TP concentrations and fluxes of the UK were investigated by trend and change point analyses. Overall UK main effects plots, annual average TRP and TP concentration have showed declines since 1984 and 1985, for TRP and TP respectively. The peak years for the main effects plots of the annual average fluxes (with covariate) were 1985 for both TRP and TP, and showed similar declines to as for the concentration main effects. The peak years in mid-1980s and the following declines in all the results can be linked to the diminishing fertilizers inputs. UK agriculture modernized with the emerging industrial methods after the World War II, and therewith, fertilizer consumptions rose dramatically (Holderness, 1985; Booth, 1998). According to the data published by the British Survey of Fertilizer (Defra, 2015), the use of of phosphate fertilizer usage/phosphate in Great Britain peaked in year 1984 at 217.530 ktonnes P/yr and have been in decline since that year (see Figure 2.29). Fertilizer consumptions displayed a decrease in 1993 at 155.6 ktonnes P/yr, and has been significantly declining from 188.9 ktonnes P/yr in 1997 to 82.387 ktonnes P/yr in 2012.

Fertilizers usage has declined from 217.530 ktonnes/yr in 1984 to 82.387 ktonnes/yr in 2012 which corresponds to a 62% decline. Despite the dramatic decline in fertilizer inputs, TRP fluxes have not been decreasing with the same high rate. TRP flux has declined from 33.523 ktonnes/yr in 1985 to 16.481 ktonnes/yr in 2012 by a 50% decline rate; the ratio of TRP flux to fertilizer consumption was 0.15 in 1984 and 0.20 in 2012. On the other hand, TP flux has declined from 84.288 ktonnes/yr in 1985 to 29.643 ktonnes/yr in 2012, corresponding to a 64% decline; the

ratio of TP flux to fertilizer consumption was 0.38 in 1984 and 0.36 in 2012. This indicates that TP flux is much more parallel to fertilizer consumption and one potential cause of this matter can be the accumulated P serving as “legacy phosphorus” (Waldrip, et al., 2015). When nutrient inputs are greater than outputs, biological controls are overwhelmed and this leads to the formation of inorganic complexes with nutrients in solid phases that are tightly bound to soil (Sharpley, et al., 2006; Dodds, et al., 2010). Phosphorus in soils is usually strongly buffered, however, when a concentration threshold is exceeded, P losses might become important (Heckrath, et al., 1995). Therefore, the legacy P can mask the consequences of the conservation measures and actions taken to reduce P levels (Hamilton, 2012; Meal, et al., 2010). Since TP represents all forms of phosphorus, it can be linked to the legacy phosphorus and can explain why TP flux decline has a higher rate than TRP flux and is parallel to the decline in fertilizer inputs.



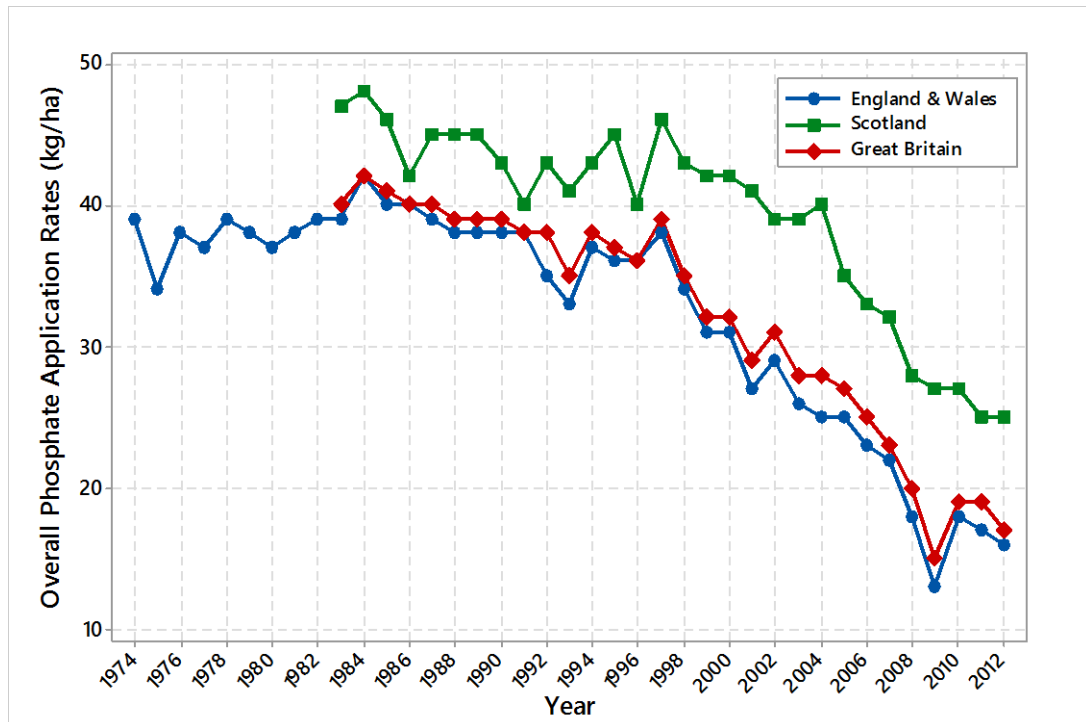


Figure 2.29 Overall phosphate application rates (kg/ha), England & Wales 1974 - 2012 and Scotland and Great Britain 1983 – 2014 (Data source: *The British Survey of Fertilizer Practise*, Defra, 2015)

The main effects of annual average TRP concentration (Figure 2.2), displayed a considerably decrease in the year 1994, furthermore, an even sharper decrease was observed in annual average TP concentration main effects for the same year. One of the possible contributors to this decrease can be the decrease in fertilizer inputs for the year 1993. However, as a more important contributor, the decline in TRP and TP concentrations can be ascribed to the improved sewage treatment provisions as the consequence of implementation of the Urban Waste Water Directive (UWWTD) (European Commission, 1991). As a result of the UWWTD, numerous actions have been executed for the reduction of direct phosphorus inputs into rivers from effluents of STWs (Defra, 2002; Neal, et al., 2010a), including provisions on secondary

treatment (eg. activated sludge process) and installations of Phosphorus stripping units as tertiary treatment. Nevertheless, it should be noted that concentrations of TRP and TP started decrease in the mid-1980s, before the implementation of UWWT directive.

The results for trend analyses indicated that most of the sites have declining trends for both TRP and TP concentrations and fluxes for the overall study period of 1974 – 2012. On the other hand, trend analysis for the last decade of the study period revealed that even though the concentration trends of TRP and TP are negative for most of the sites, the number of sites having positive trends in both TRP and TP are higher than those having negative trends, and thus, it may suggest that average flow has increased over the period 2003-2012. Another possible explanation could be the population growth and its increasing pressure to sewage treatment works by counteracting the former measures taken under UWWTD.

Change point analyses indicated that most of the records indicated significant step changes. Understanding the driving forces behind these step changes is a complex issue; they cannot easily be attributed to linear drivers unless evident threshold outcomes exist. The positions of most of the step changes are in downward trends in time series, therefore one possible cause leading to the step changes might be the droughts encountered within the study period. On the other hand, droughts would be followed by a recovery and thus, the effect sizes of the steps caused by droughts would be small. However, our results indicated that most of the significant step changes in TRP concentration had large effect sizes (in the range of 0.91 - 1.00)

(Figure 2.14). Also, several droughts that affected the UK have been listed by (Hannaford, 2015) for the years 1990 - 1992, and 1995 - 1997 but none for 2000s, whereas there are many step changes encountered in 2000s in our results (Figure 2.28). Therefore, step changes encountered in this study cannot be explained by droughts.

Comparing the geometric means of the effect sizes of concentration and flux records, it can be asserted that the actual step change is in concentration data and variations in flow can restrict step changes calculated for the flux records, resulting in fewer change points and lower effect sizes than the concentration records. The proportions of decrease in TRP concentration due to the step change were in the range of 0.68% and 89% with a geometric mean of 22%, with the rest of the decrease accounted by the background downward trend. Given that, step changes can be accounted as important contributors to the overall decreasing trends. Due to the lack of TP records in the monitoring database, the number of sites having significant step changes for TP concentration and flux are quite low and thus, it is difficult to make interpretations on the step changes of TP.

Given that most of the step changes in TRP concentration were encountered in the period of 1993 - 1997 (Figure 2.13) and no droughts were encountered in that period, these step changes can either be explained with the significant decrease of fertilizer inputs since 1993, or as a result of implementation of the UWWTD. Spatial distribution maps indicated that TRP concentration step changes encountered in the period 1993-1997 were mostly from urbanized regions such as Midlands, Wales,

North West and South East England regions, whereas in less urbanized regions like Northern Scotland and South East England mostly has step changes in different periods or has seen no change. Therefore, it can be proposed that these steps were brought by the implementation of the UWWTD.

## **Chapter 3:**

### **Case Studies on Five Catchments**

#### **3.1. Introduction**

In this chapter, a further analysis was performed by considering case studies that represent different catchment characteristics for a better understanding of the underlying contributors of riverine phosphorus levels. Chapter 2 indicated that there were many significant step changes in TRP concentration time series and most of these step changes were detected in the period 1993-1997 which suggested that the implementation of Urban Waste Water Treatment Directive (UWWTD) was the key factor leading to the step changes. To test this hypothesis, firstly the records of the discharges from sewage treatment works were checked using the datasets obtained from the Environment Agency. However, in most of those records, phosphorus data was neither available at all, nor sufficient enough to analyse. Therefore, as an alternative approach, Principle Component Analysis (PCA) was employed in this Chapter with an aim of tracking down the urban source or other source contributors with different case examples.

### 3.2. Selection of Sites

The examples were chosen based on three parameters; trend type (negative, positive or no trend), step change (with or without a step change) and catchment type (rural or urban river). Therefore, there were 12 possible combinations of characteristics that could identify a catchment as given in Table 3.1.

*Table 3.1 Descriptions of categorical codes used in catchment identifications for selection of case examples*

Categorical code	Scenario
1	Rural river with a step change and negative trend
2	Rural river with a step change and positive trend
3	Urban river with a step change and negative trend
4	Urban river with a step change and positive trend
5	Rural river with no step change and negative trend
6	Rural river with no step change and positive trend
7	Urban river with no step change and negative trend
8	Urban river with no step change and positive trend
9	Rural river with step change and no trend
10	Urban river with step change and no trend
11	Rural river with no step change and no trend
12	Urban river with no step change and no trend

*Table 3.2 Summary of catchment characteristics based on TRP concentration data for trend and step change analyses.*

Region	River Name	Site ID	Land Use		Length of records	No. of STWs	Step Change		Trend			Land Type		Categorical Code
			Arable %	Urban %			Yes	No	Positive	Negative	No	Rural	Urban	
NW	Irwell	1003	2.8	26	35	5	X			X			X	3
NW	Weaver	1005	22.5	10	28	9		X	X				X	8
NW	Alt	1006	38.2	31.6	28	3	X			X			X	3
NW	Wyre	1010	10.5	3.9	22	2		X		X		X		5
NW	Kent	1012	5.6	3.4	24	3	X			X		X		1
NW	Douglas	1015	18.8	25.9	28	6		X	X				X	8
NW	Darwen	1016	-	-	30	1		X	X			-	-	-
NW	Eamont	1018	3.2	2.1	23	1	X			X		X		1
NW	Lyne	1021	8.7	1	17	1		X		X		X		5
NE	Coquet	2009	-	-	18	2		X		X		-	-	-
NE	Wansbeck	2012	25.1	2.2	20	2	X			X		X		1
NE	South Tyne	2021	-	-	22	1		X			X	-	-	-
NE	Wear	2044	-	-	21	24	X			X		-	-	-
MI	Idle	3009	50.1	15.3	27	17	X			X			X	3
MI	Soar	3010	-	-	23	17	X			X		-	-	-
MI	Sowe	3014	32.1	15.9	26	1	X			X			X	3
MI	Dove	3015	14.6	4.2	25	13	X			X		X		1
MI	Tern	3019	43.4	7	26	9		X		X		X		5
MI	Terne	3029	24.6	2.7	27	7	X			X		X		1
NE	Hull	4001	71.7	2.1	19	7	X			X		X		1
NE	Dearne	4009	68.8	6.9	14	10		X		X		X		5
NE	Wharfe	4013	9.2	4.5	18	9	X			X		X		1
AN	Witham	5410	67.1	6.8	7	22		X		X		X		5
AN	Ely Ouse	5651	-	-	11	1		X		X		-	-	-
AN	Wensum	5714	71.3	3.1	17	5	X			X		X		1
AN	Bure	5722	71.3	3.1	17	6	X			X		X		1
TH	Kennet	6004	43.2	7.1	25	1	X			X		X		1
TH	Loddon	6005	23.1	27.3	14	1		X		X			X	8
TH	Wey	6008	23.5	16	16	3	X			X			X	3
SO	Medway	7001	27.4	12.3	32	28	X			X			X	3
SO	Cuckmere	7005	20.2	8.3	28	1		X	X			X		6
SO	Arun	7008	-	-	25	7	X			X		-	-	-
SW	Tone	8326	36.1	9.1	10	2		X	X			X		6
SW	Frome	8400	45.7	3.6	18	6	X			X		X		1
SW	Parret	8426	45.1	5.8	19	12	X			X		X		1
SW	Axe	9001	30.8	3.4	26	6		X		X		X		5
SW	Otter	9002	35.8	7	29	3	X			X		X		1
SW	Dart	9011	7.6	3.1	21	3	X			X		X		1
SW	Plym	9014	6.3	3.6	29	1	X			X		X		1
SW	Tavy	9015	6	3.5	21	1	X			X		X		1
SW	Lynher	9023	20.9	3.4	19	1		X		X		X		5
SW	Fal	9025	-	-	32	3	X			X		-	-	-
SW	Carnon	9026	21.5	10.6	32	1		X	X				X	8
SW	Camel	9027	14.9	4.4	22	6		X		X		X		5
SW	Yeo	9035	11.4	1.7	20	5	X			X		X		1
SEPA EAST	Devon	14002	9.5	3.6	21	7		X		X		X		5

Since an analysis on the data of the catchments with multiple HMS sampling sites would be rather complex and time consuming, only those catchments having just one sampling site were taken into consideration for selection of the case examples. According to these criteria, 47 catchments were found to be suitable for

categorisation and those catchments are listed in Table 3.2 with their characteristics and corresponding categorical codes. For the definition of the river land type, catchments with urban land use percentage equal or greater than 10% were defined as urban rivers and those less than 10% were defined as rural rivers. There were no land use information for some catchments and thus they were excluded from the selection. The results for both concentration and flux trend and step change analysis fall into same categories in each chosen catchment, i.e. having a negative trend and a step change in both concentration and flux time series. Not each and every category was represented by a catchment; only 5 possible combinations could be found within the available dataset. Catchments having the highest length of records were selected for the 5 scenarios and listed in Table 3.3.

*Table 3.3 Selected catchments for 5 case examples for further analysis*

Categorical code	Scenario	HMS code	River Name	Length of record (yr)
1	Rural river with a step change and negative trend	9002	Otter	29
3	Urban river with a step change and negative trend	1003	Irwell	35
5	Rural river with no step change and negative trend	3019	Tern	26
6	Rural river with no step change and positive trend	7005	Cuckmere	28
8	Urban river with no step change and positive trend	9026	Carnon	32



### **3.3. Methodology**

#### **3.3.1. Principal Component Analysis**

Water quality data from each site were analysed using Principal Component Analysis (PCA) technique for identification of end-members. PCA is a multivariate analysis technique that has the capability of data reduction; large datasets can be reduced to smaller sets of factors or components via detection of interrelations (Melloul & Collin , 1992). Application of PCA in hydrological data allows the measured variables to be expressed as linear combinations of uncorrelated and not directly observable principle components that can be explained as influences or key processes (Haag & Westrich, 2002; Lischeid & Bittersohl, 2008). An alternative to PCA is a similar method referred as Factor analysis (FA) and the choice of using PCA or FA depends on the purpose of the study (Gordon, et al., 2004). PCA is considered to be a “closed model” where all the variance is accounted for, on the other hand FA is more like an “open model” in which part of the variance is reserved for variables that may yet be included. As it is more suitable for our purpose of the study, PCA was chosen as the method of choice.

The procedure of PCA involves transformation of the dataset to a new coordinate system in which the new axes are in the direction of the largest variance within the data. The first principle component is accounted for the greatest variance within the data, the second principle component for the second greatest variance, and so on. A PCA approach was used because it was believed that for each site a principal component would arise that could be identified as being and urban

wastewater component and that this component could be tracked relative to any step change so as to assess whether the step change coincided with a step change in that principal component. *A priori* we can hypothesize that any principal component associated with urban wastewater would have a high loading for conductivity, BOD, suspended solids and P, but a lower loading for nitrate.

The PCA technique was applied to all the data available in the database (not only annual average values) within the context of the study period of 1974 - 2012 using the variables; Total reactive phosphorus (TRP), Suspended solids, Biological oxygen demand (BOD), Nitrate and Conductivity. Each variable was z-transformed prior to analysis for standardization of the units;

$$z = \frac{(x - \bar{x})}{\sigma} \quad (3.1)$$

where  $x$  is the measured value of the variable,  $\bar{x}$  is the dataset mean of the variable and  $\sigma$  is the standard deviation. In this study, PCAs were performed using the commercially available MINITAB v17 statistical software package and covariance matrix was chosen for analysis. Only the principal components with an eigenvalue  $>1$  and the first with and eigenvalue  $<1$  were taken into consideration in the analysis (Worrall, et al., 2012).

### **3.4. Results & Discussions**

#### **3.4.1. River Irwell**

##### ***3.4.1.1. Catchment Characteristics***

The River Irwell is a 39 mile (63 km) long river flowing between the counties Lancashire and Greater Manchester in North West England. The Irwell catchment area is 715 km<sup>2</sup> covering the towns of Manchester, Bolton, Oldham, Salford and Rochdale. Its main tributaries are the rivers Roch, Croal, Medlock and Irk which flow into the Manchester Ship Canal via Irwell (Environment Agency, 2009). Irwell's underlying geology is consisted of Lower Coal Measures overlying Millstone Grit where both of which are under limestone rocks from Carboniferous period. The surface deposits are comprised of thick peat in upper reaches and glacial boulder, glacial sand and gravel in the lower reaches (Gaskell, 2011).

The Irwell is a mostly an urban catchment and has a legacy from heavy industry that has been growing since the industrial revolution in North West England. It has been degraded heavily by the chemicals in the effluents of many industries such as paper, printing, coal, cotton, bleaching etc. and as a result, a very limited natural habitat remains in Irwell today (Environment Agency, 2009).

### **3.4.1.2 Results**

Irwell's annual average TRP concentration time series (Figure 3.1) displayed two peaks; one in year 1984 and the other in 1996 and also a sharp decrease in 1994. This decrease can be correlated with the implementation of the UWWTD in 1992. After the downfall, concentration increased dramatically until 1996 and has been declining since. Change point analysis indicated significant step changes; the year before change was 1997 with a probability of 0.9999 for concentration, and the year before change was recorded as 2000 with a probability of 0.9995 for flux. The delay of the step change in flux can be attributed to the increased water yield resulting in a higher TRP flux; extreme flowrates were recorded as 63.3 m<sup>3</sup>/s in January and 62.2 m<sup>3</sup>/s in March 2000 while the average catchment flowrate was 16.5 m<sup>3</sup>/s for the overall study period. These extreme values shifted the flux step change with respect to the concentration step change.

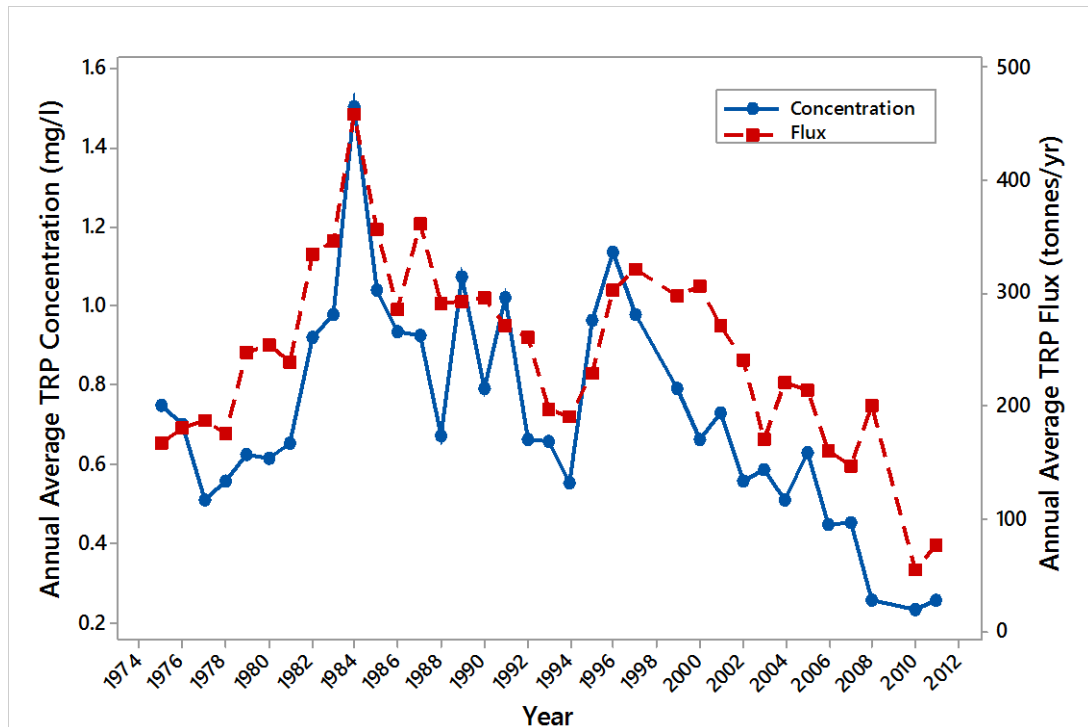


Figure 3.1 Annual average TRP Concentration and Flux time series of River Irwell at Salford

#### 3.4.1.2.a. Principal Component Analysis

Principal component analysis was applied to all the data available within the study period in the database. All components with eigenvalue  $>1$  plus the first with an eigenvalue  $<1$  were accepted; three principal components (PCs) were accepted according to this rule (Table 3.4) and a cumulative variance of 68.9% was explained by these PCs. The first component (PC1) had a quite high loading on conductivity, along with high loadings on TRP concentration and nitrate concentration. The PC2 had a negative high loading on BOD concentration and positive high loadings on suspended solids and nitrate concentration; and a low loading on conductivity. The

third component was characterised by a positive high loading on suspended solids concentration and a negative high loading on TRP concentration, with the rest of the variables also having relatively high loadings.

*Table 3.4 PCA results on River Irwell, showing the principal components with eigenvalues > 1 and the first component coming after with an eigenvalue < 1.*

<b>Variable</b>	<b>PC1</b>	<b>PC2</b>	<b>PC3</b>
TRP Concentration	0.525	-0.207	-0.520
Suspended Solids Concentration	0.088	0.474	0.632
BOD Concentration	0.253	-0.699	0.382
Nitrate Concentration	0.369	0.484	-0.342
Conductivity	0.719	-0.096	-0.261
<i>Eigenvalue</i>	1.2565	1.1742	0.9203
<i>Cumulative variation explained (%)</i>	25.7	49.8	68.6

For a better understanding of the patterns and relationships within the dataset, the scores of the first three principal components were plotted against one another and matrix plot is given (Figure 3.2). PC3 versus PC2 plot in Figure 3.3 suggested that there could be trends in the data, therefore it was investigated in a higher resolution in Figure 3.3.

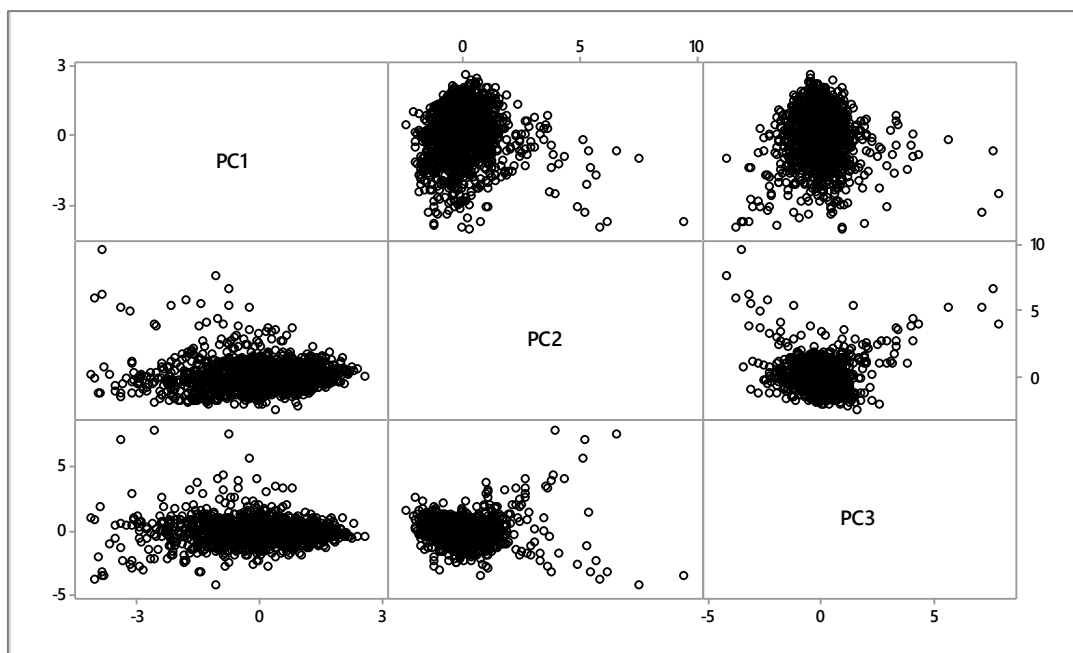
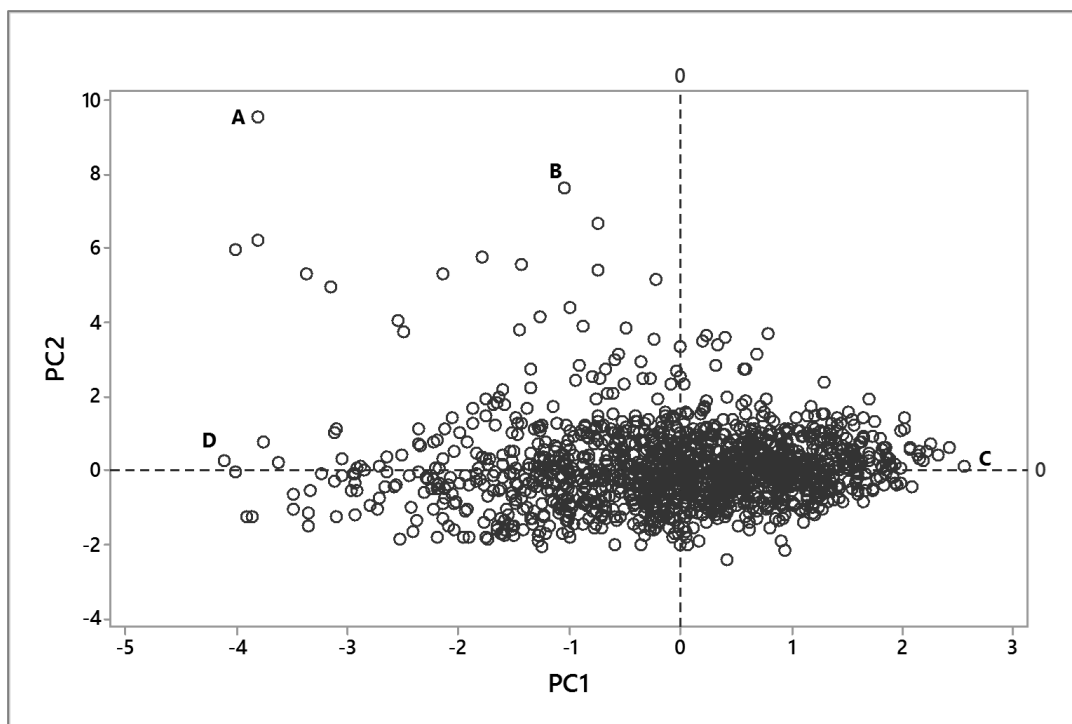


Figure 3.2 Matrix plot for comparisons of principal components on the entire dataset of River Irwell

Figure 3.3 suggested that there could be three trends with the dominant trend CD parallel to PC1. The end member A represents the highest BOD concentration in the whole dataset with 61 mg/l, while the TRP concentration for the same sample was 0.1 mg/l. Another end member was point B with the highest suspended solids concentration of 545 mg/l with a low record of nitrate concentration for the same point. The end member C was a nitrate concentration with 6.83 mg/l with and end member D was with the highest TRP concentration of 3.90 mg/l.



*Figure 3.3 PC1 vs PC2 scores for the entire dataset of River Irwell*

PC3 versus PC2 scores were compared in Figure 3.4. The end member E corresponded to the same point A in Figure 3.3 with the highest BOD concentration and similarly, point F represented the same point of highest suspended solids concentration in Point B (Figure 3.3). The end member G corresponded to a high nitrate concentration of 6.93 mg/l and end member H represented the highest conductivity in the entire dataset with a value of 1850  $\mu\text{S}/\text{cm}$ .



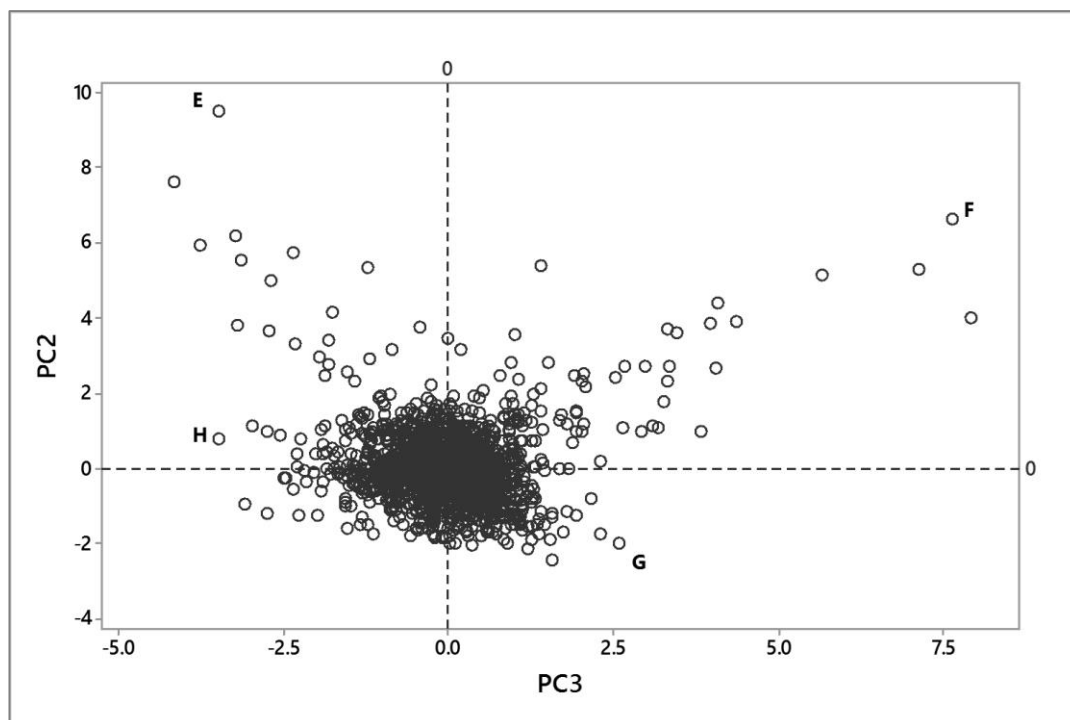


Figure 3.4 PC3 vs PC2 scores for the entire dataset of River Irwell

#### 3.4.1.2.b. Principle Component Analysis Pre and Post Step Change

Principal component analysis was also performed regarding the step change; the data before and after the change point were analysed individually. All components with eigenvalue  $>1$  plus the first with an eigenvalue  $<1$  were accepted; three principal components (PCs) defined according to this rule (Table 3.5). A cumulative variation of 71.4% for the data pre-change point and 79% variation for the post-change point data were explained by the PCs. The first principal component on the pre-change point data had high loadings on all components except BOD concentration. Conversely, PC2 had a very high loading on BOD concentration and another high loading on Conductivity. PC3 had a very high loading on suspended solids concentration and another high loading on TRP concentration. For the post-change point data, PC1 had similar loadings with the one in pre-change point, but the

loadings became less on BOD and suspended solids concentrations. The loading on BOD concentration increased even more with PC2 and also PC3 on post-change point data. High TRP concentration loading decreased with PC3 in the post-change point data and also changed its sign.

*Table 3.5 PCA results on River Irwell – pre and post step change, showing the principal components with eigenvalues > 1 and the first component coming after with an eigenvalue <1*

<b>Variable</b>	<b><i>Pre step change</i></b>			<b><i>Post step change</i></b>		
	<b>PC1</b>	<b>PC2</b>	<b>PC3</b>	<b>PC1</b>	<b>PC2</b>	<b>PC3</b>
TRP Concentration	0.524	0.046	0.523	0.544	-0.194	-0.111
Suspended Solids Concentration	-0.460	0.287	0.792	-0.340	-0.298	-0.882
BOD Concentration	-0.109	0.813	-0.292	-0.043	-0.908	0.345
Nitrate Concentration	0.568	-0.029	0.118	0.534	0.122	-0.154
Conductivity	0.424	0.503	-0.021	0.549	-0.183	-0.259
<i>Eigenvalue</i>	1.6614	1.1072	0.7997	2.0534	1.0478	0.8491
<i>Cumulative variation explained (%)</i>	0.332	0.554	0.714	0.411	0.620	0.790

Comparisons of PC scores before and after step change for each variable are displayed (Figure 3.5). It can be observed that PC2 was not influenced by the step change in any variable, whereas PC1 and PC3 had dramatic changes after the step. The PC1 score of suspended solids concentration and PC3 score of BOD concentration had the most substantial changes after the step change.

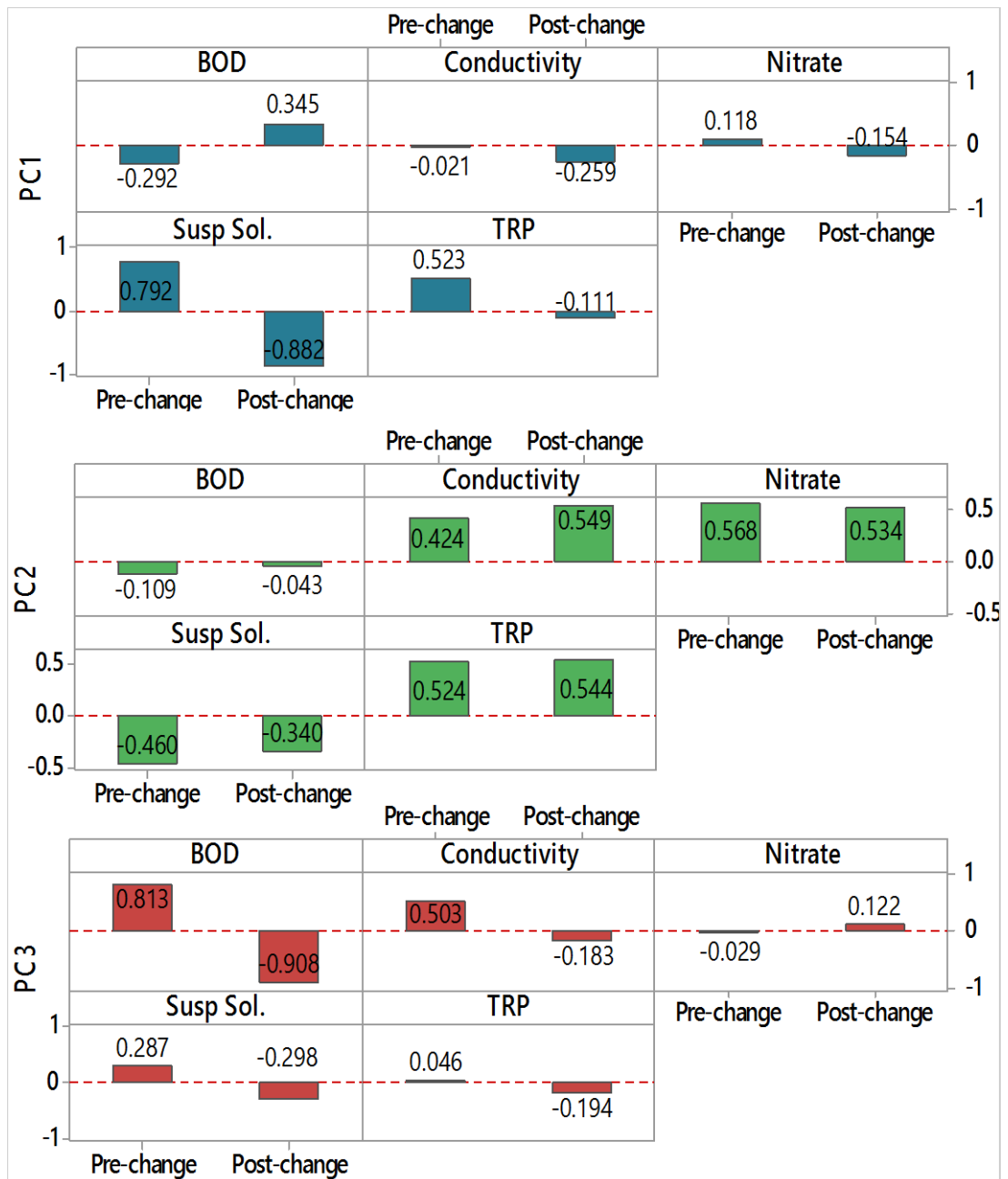


Figure 3.5 Comparisons of pre and post step change principal components for each variable on the data of River Irwell

Matrix plots of the principal components are displayed (Figure 3.6). Comparisons for the pre and post step change principal components indicated distorted structures after the step change.

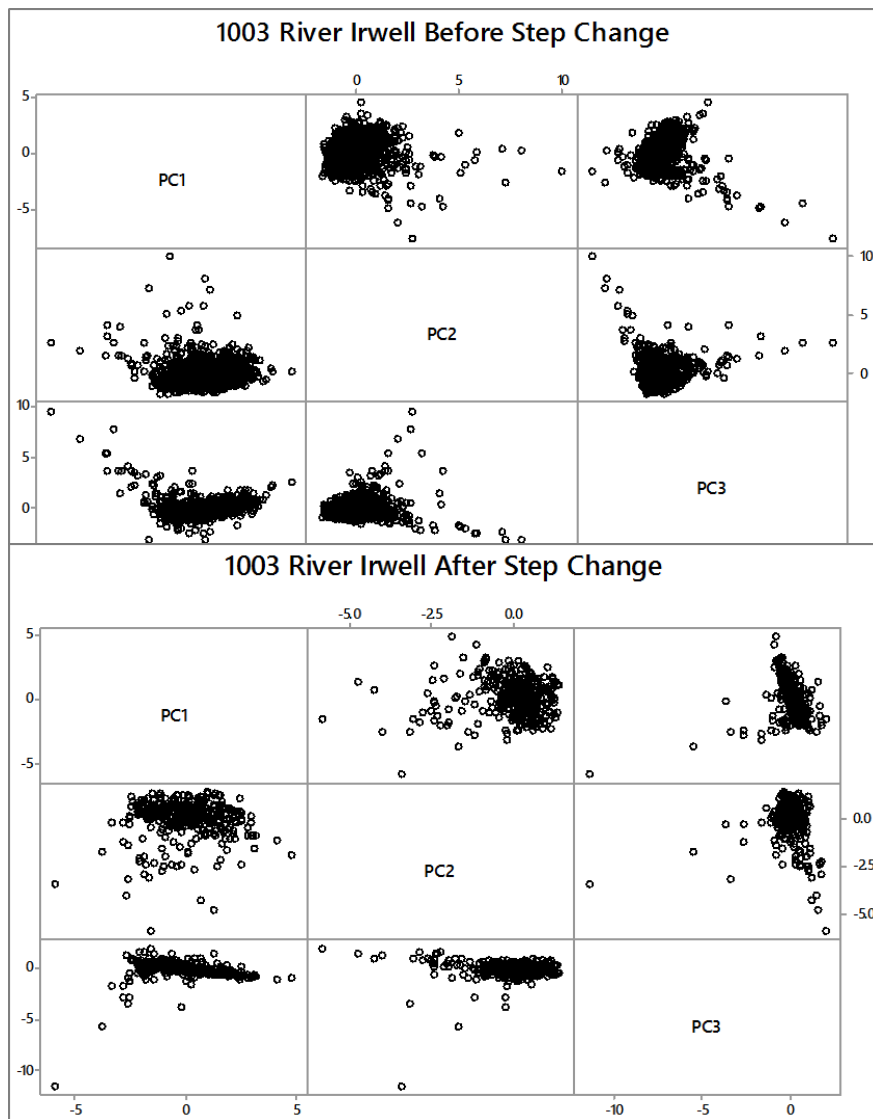
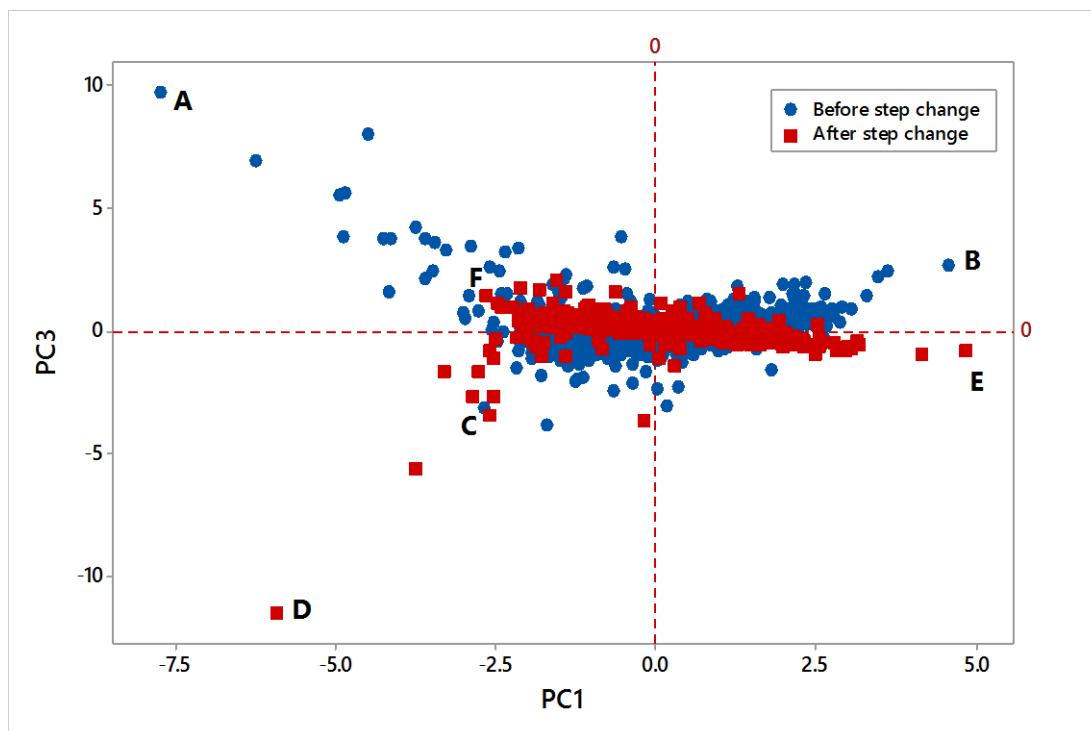


Figure 3.6 Matrix plot of principal components on the dataset of River Irwell - pre and post step change

Pre and post step change plots of PC2 versus PC3 were further compared (Figure 3.7). The end member A of the pre-step change scores represented a high suspended solids concentration of 545 mg/l. Another end member B corresponded to a high TRP concentration of 3.9 mg/l, and end member C represented a high BOD concentration of 52 mg/l. One of the end members of the post-change point scores

was point D with a high suspended solids concentration of 436 mg/l. Other end members of the post-change scores were point E with a high TRP concentration of 2.28 mg/l and point F with high BOD value of 12.5 mg/l.



*Figure 3.7 PC1 vs PC3 scores compared for the pre and post step change data of River Irwell*

### **3.4.1.3. Discussion**

The results of the principal component analysis on the entire dataset of River Irwell showed that both PC1 and PC2 equally contribute to the total variation explained with approximately 25% variation each (Table 3.4). PC1 showed a strong influence on conductivity and also TRP concentration, but not on suspended solids concentration suggesting that PC1 might be representing a source as sewage effluent. PC2 had a strong negative influence on BOD concentration along with positive and

equally high loadings on suspended solids and nitrate concentration, but with no loading on conductivity. Therefore, PC2 could be identified as a diffuse source such as agricultural run-off. The end member A in Figure 3.3 represented a high BOD concentration and indicated that BOD concentration increases with respect to both PC1 and PC2. Other end members TRP and nitrate concentrations were represented by points C and D, and showed that most of the data from these variables are parallel to PC1 which is defined as sewage sources, and does not change much with respect to PC2 which is the diffuse agricultural source. This is an expected result from Irwell as a catchment with a highly urban character. PC3 explained 19% of the total variation explained, and had the highest loading on suspended solids concentration with a strong negative influence on TRP concentration. Given that information, it is difficult to identify the source of PC3, but possible interpretations could be a groundwater source or storm water run-off. Figure 3.4 suggested that BOD concentration (point E – Figure 3.4) was increasing both with PC2 and PC3. Suspended solids concentration (point F – Figure 3.4) was also increasing with respect to both PC2 and PC3, but was closer to PC3.

#### ***3.4.1.3.a. The step change***

A comparison among the principal component analysis scores of the pre and post step change records (Figure 3.5) showed that there was no impact of the step change on PC2, so it is not likely to be related to a sewage effluent source. The greatest changes were on the loadings of PC1 on suspended solids and TRP concentration and the loadings of PC3 on BOD concentration and conductivity. Given that it could be said that most of the changes in PC1 and PC3 loadings were

improvements in water quality and concentrations began to decrease after the step change. This can be interpreted as an accomplished result of the implementation of the UWWTD on a river with a highly urban character.

### **3.4.2. River Tern**

#### ***3.4.2.1. Catchment Characteristics***

The River Tern (historical name Tearne) rises from the small lake in north eastern Shropshire, and flows south west by Market-Drayton. It is then joined by River Meese and Roden until flowing into the River Severn between Atcham and Wroxeter. The whole course of the catchment is approximately 30 miles and it is the longest of the Shropshire streams.

The catchment has a complex geology; contains different lithologies from the upper Carboniferous to lower Jurassic clays. With its two main tributaries, the River Tern lies on Rhaetic and Liassic clays and mudstones or Permo-Triassic Sherwood sandstones of the North Shropshire Plain. The catchment is mainly rural and free of large urban areas. Nevertheless, human activity over the years have degraded the flora and fauna near Tern and Strine areas. Intensive agricultural activities with land uses of grassland, vegetables, woodland, and root crops are present in the catchment area. Also, industrial activities with dairy and sugar beet factories located in the lower catchment area are potential sources of water quality degradation (Adams, 2003).

#### ***3.4.2.2. Results***

Annual average TRP concentration time series of River Tern (Figure 3.8) displayed two peaks in years 1990 and 1997, however these peaks do not overlap with the peaks in years 1988 and 1998 in flux time series. The reason for the shifts



can be explained by increased water yields in those years; extreme flowrates were recorded as 36.8 m<sup>3</sup>/s in January 1988 and 39.9 m<sup>3</sup>/s in January 1998 while the average flowrate was 6.48 m<sup>3</sup>/s for the catchment in overall study period. Change point analysis results were found to not be statistically significant after familywise correction; the year before step in 1998 with a probability of 0.9912 and 1990 with a probability of 0.9950 for TRP concentration and flux, respectively.

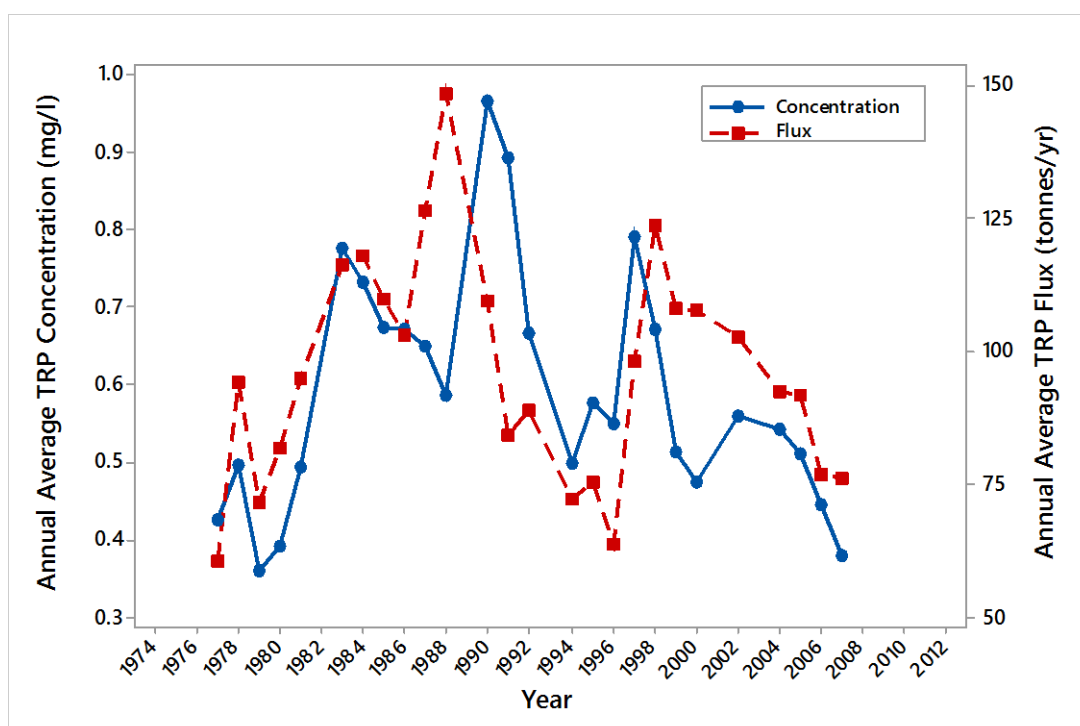


Figure 3.8 Annual average TRP Concentration and Flux time series of River Tern at Atcham

#### 3.4.2.2.a. Principal Component Analysis

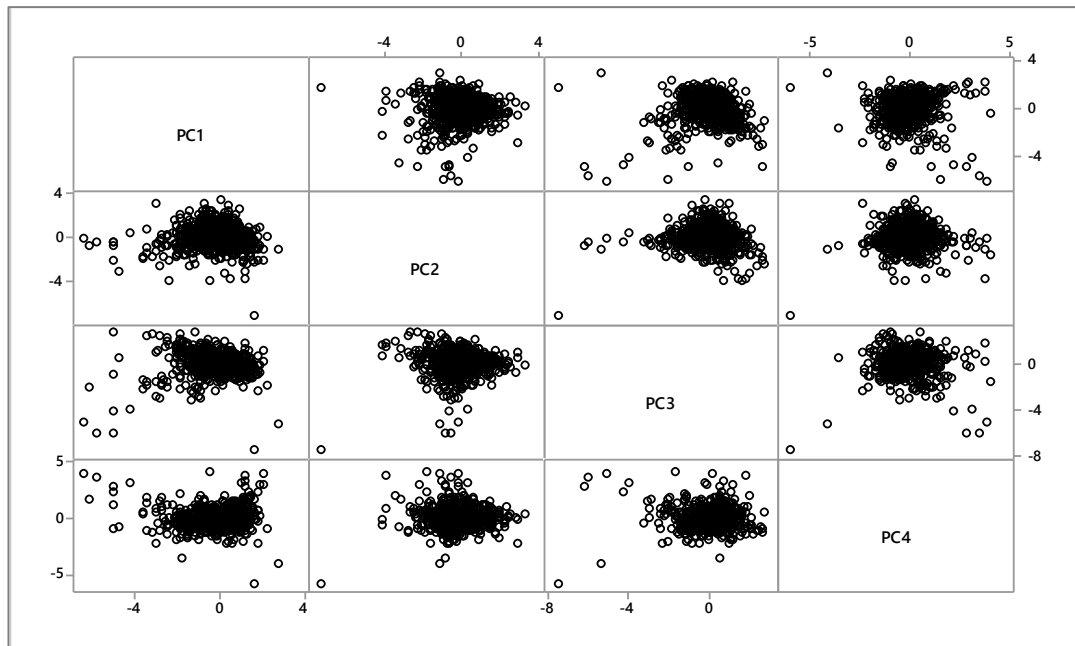
Four components with an eigenvalue >1 plus the first with an eigenvalue <1 were accepted for analysis and a cumulative variation of 84.5% was explained by these components (Table 3.6). The first component had high loadings in all variables except conductivity; quite high negative loadings were observed on suspended solids

and BOD concentrations. In contrast, PC2 had a very high loading on conductivity and a negative high loading on nitrate concentration. PC3 had negative high loadings on TRP and suspended solids concentrations with a positive high loading on BOD concentration. The fourth component had a negative high loading on TRP concentration and a positive high loading on nitrate concentration.

*Table 3.6 PCA results on River Tern, showing the principal components with eigenvalues > 1 and the first component coming after with an eigenvalue < 1.*

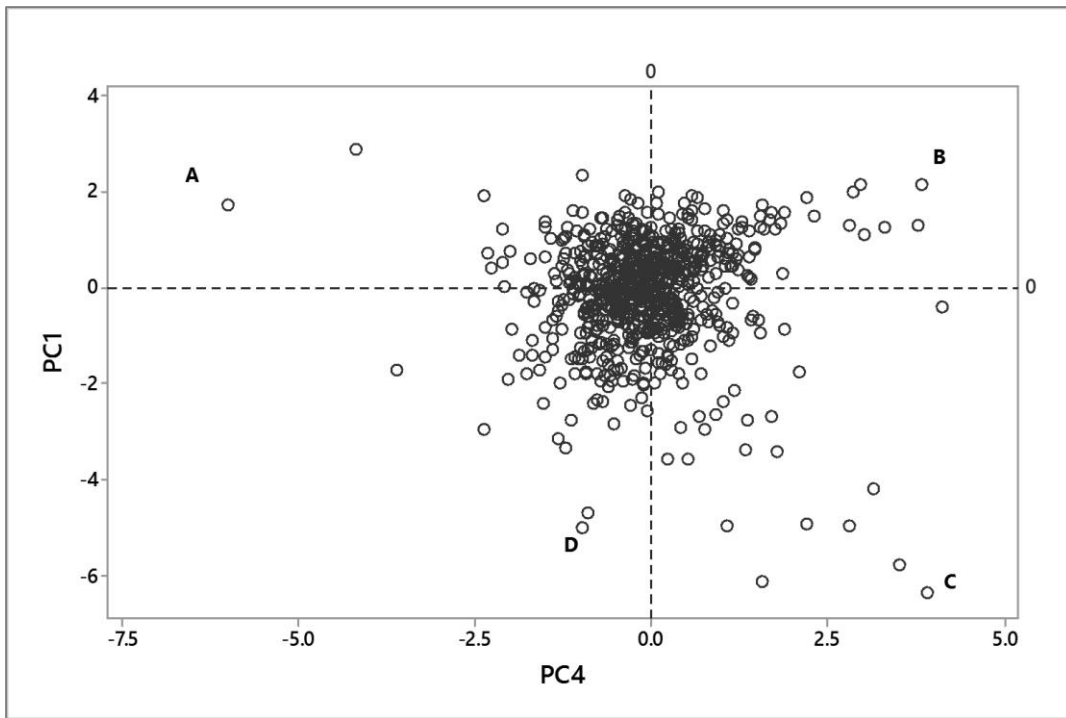
<b>Variable</b>	<b>PC1</b>	<b>PC2</b>	<b>PC3</b>	<b>PC4</b>
TRP Concentration	0.354	-0.312	-0.546	-0.562
Suspended Solids Concentration	-0.647	-0.150	-0.627	0.383
BOD Concentration	-0.501	-0.311	0.537	-0.282
Nitrate Concentration	0.439	-0.503	0.139	0.655
Conductivity	0.108	0.728	-0.038	0.170
<i>Eigenvalue</i>	1.3523	1.1140	1.0791	0.8493
<i>Cumulative variation explained (%)</i>	26.0	47.4	68.1	84.5

The scores of the first four principal components were plotted against one another and matrix plot is given (Figure 3.9). PC4 versus PC1 plot (Figure 3.10) and PC2 versus PC3 plot (Figure 3.11) were examined.



*Figure 3.9 Matrix plot for comparisons of principal components on River Tern*

The end member A in Figure 3.10 represented the highest TRP concentration in the whole dataset with 4.8 mg/l. Another end member was point B with the highest nitrate concentration of 23 mg/l with a low record of BOD concentration for the same point. The end member C was the highest suspended solids concentration with 240 mg/l with and the last end member D was with the highest BOD concentration with a value of 9 mg/l.



*Figure 3.10 PC4 vs PC1 scores for the entire dataset of River Tern*

PC2 versus PC3 scores were compared in Figure 3.11. The end member E corresponded to a high nitrate concentration of 15.1 mg/l and point F represented the highest conductivity of the entire dataset with a value of 900  $\mu\text{S}/\text{cm}$ . The end member G corresponded to a high suspended solids concentration with a value of 228 mg/l.

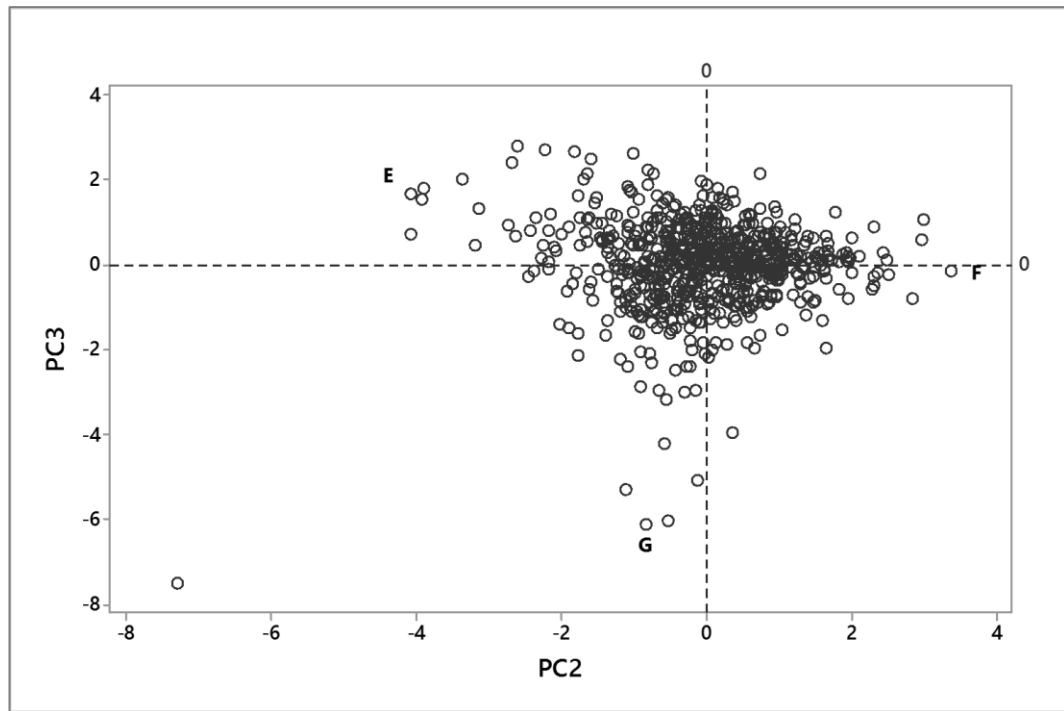


Figure 3.11 PC2 vs PC3 scores for the entire dataset of River Tern

#### 3.4.2.3. Discussion

It is difficult to interpret the results for River Tern with the four principle components defined. The first component explained 26% of the total variance and showed strong negative loadings on suspended solids and BOD concentrations along with a strong positive loading on nitrate and a moderate positive loading on TRP concentration. Given that and Tern being a highly rural catchment with intense agricultural activities, PC1 was defined as a diffuse source with agricultural run-off. PC2 explained 21.4% of the dataset variation. All the variables were negatively correlated with PC2 expect for the highly strong correlation with conductivity indicating that it could be an urban sewage source. The third component explained 20.7% of the total variance and had strong negative influences on suspended solids and TRP concentrations and a positive strong influence on BOD concentration and

no influence on conductivity. These findings suggest that PC3 cannot be point or diffuse source, rather it could be related to a groundwater source contribution although that would not explain the high BOD loading for this component. The final component PC4 explained 16% of the dataset variation with a strong positive influence on nitrate concentration. For the other variables, PC4 had a strong negative influence on TRP concentration, a moderate loading on suspended solids concentration, a small negative influence on BOD concentration and a small positive influence on conductivity. With this picture, it is hard to identify the source of PC4 completely, but regarding the high nitrate loading one possible contributor could be agricultural runoff. The end members in PC4 vs PC1 plot (Figure 3.10) were defined as TRP concentration (point A), nitrate concentration (point B), suspended solids concentration (point C) and BOD concentration (point D), whereas the end members in PC2 vs PC3 plot (Figure 3.11) were nitrate concentration (point E), conductivity (point F) and suspended solids concentration (point G). The end members indicate that the dominant variables in Tern's catchment chemistry were nitrate and suspended solids, which was expected from a highly rural catchment.

### **3.4.3. River Cuckmere**

#### ***3.4.3.1. Catchment Information***

The Cuckmere River rises from the north of Heathfield Park, in East Sussex, South East England. The name Cuckmere comes from a Saxon word meaning “fast flowing water”, as it descends 100 metres in its initial 7 km. The river eventually flows into the English Channel from the Sussex Coast.

The catchment covers an area of 137.7 km<sup>2</sup> to its tidal limit. It has a considerably variable geological cover and shows distinctive features such as an extremely narrow structure compared to its length. Along its course, cross-sections of Wealden geology from Ashdown Sandstone through Weald Clay to chalk present. Only a small portion of the catchment area is under urban development; the river mainly flows through rural countryside. The only urban areas are Horam and Heatfield (NRA, 1990).

#### ***3.4.3.2. Results***

River Cuckmere’s annual average TRP concentration and flux time series (Figure 3.12) displayed almost completely different profiles than each other. The highest peak year in concentration series corresponded to a decrease in flux and, in contrast, the year of peak in flux series was a decrease for concentration. Change point analysis results were not statistically significant after family wise correction; the year before step in 2000 with a probability of 0.9884 and 2001 with a probability of 0.9848 for TRP concentration and flux, respectively.

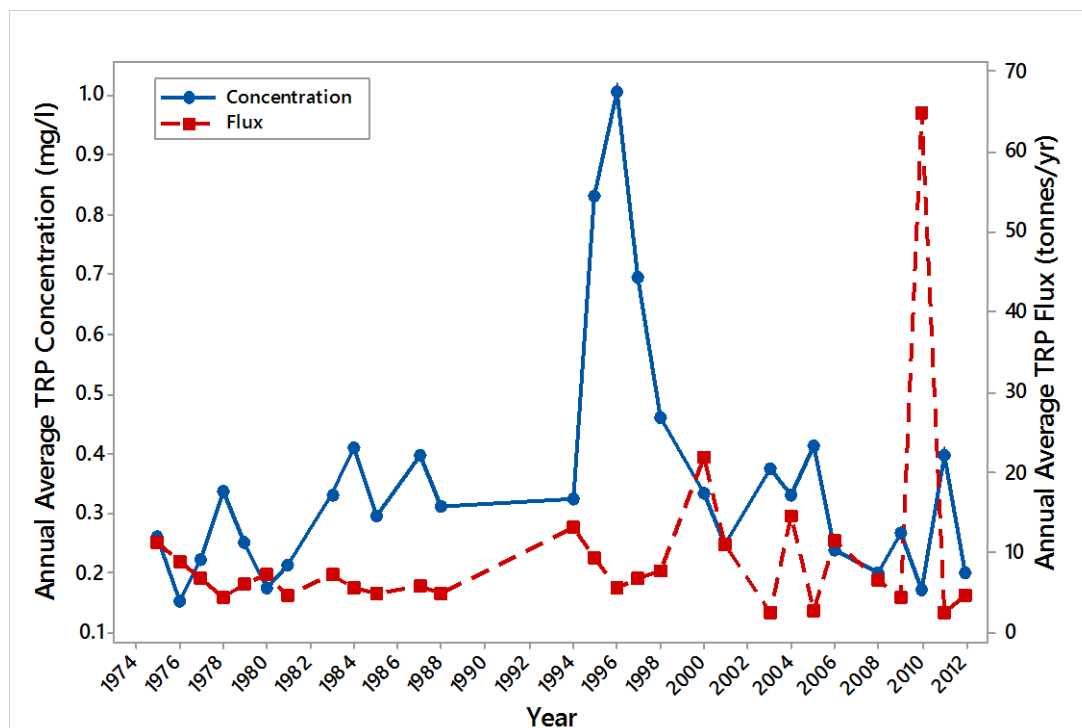


Figure 3.12 Annual average TRP Concentration and Flux time series of River Cuckmere at Shermans Bridge

#### 3.4.3.2.a. Principal Component Analysis

Three components with an eigenvalue  $>1$  plus the first with an eigenvalue  $<1$  were accepted for analysis and a cumulative variation of 66.7% was explained by these components (Table 3.7). The first component had high loadings for TRP concentration and conductivity, whereas loadings on nitrate and suspended solids concentrations were rather low. The second component had a quite high loading on nitrate concentration and also a high loading on suspended solids concentration with the rest of the variables having low loadings. Lastly, PC3 had a strong loading on BOD concentration and also a high loading on suspended solids concentration.



Table 3.7 PCA results on River Cuckmere, showing the principal components with eigenvalues  $> 1$  and the first component coming after with an eigenvalue  $< 1$ .

Variable	PC1	PC2	PC3
TRP Concentration	0.672	0.027	0.199
Suspended Solids Concentration	-0.151	0.509	0.541
BOD Concentration	-0.384	-0.198	0.716
Nitrate Concentration	0.057	0.831	-0.120
Conductivity	0.612	-0.105	0.375
<i>Eigenvalue</i>	1.3181	1.1528	0.9702
<i>Cumulative variation explained (%)</i>	25.6	47.9	66.7

The scores of the three PCs were plotted against one another and matrix plot is given (Figure 3.13). PC2 versus PC1 plot (Figure 3.14) and PC3 versus PC2 plot (Figure 3.15) were examined.

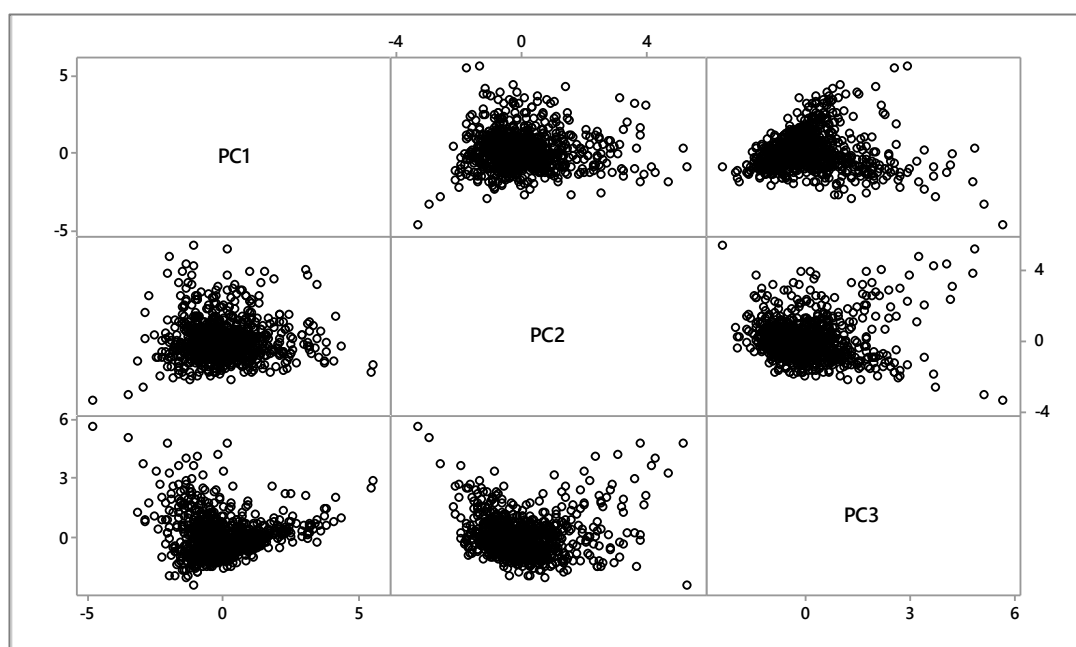


Figure 3.13 Matrix plot for comparisons of principal components on River Cuckmere

The end member A in Figure 3.14 represented the highest conductivity record in the whole dataset at 1080  $\mu\text{S}/\text{cm}$ . Point B corresponded to a high TRP concentration of 2.2 mg/l and the end member C represented a nitrate concentration with a value of 13.1 mg/l. The last end member D was with the highest BOD concentration with a value of 14 mg/l.

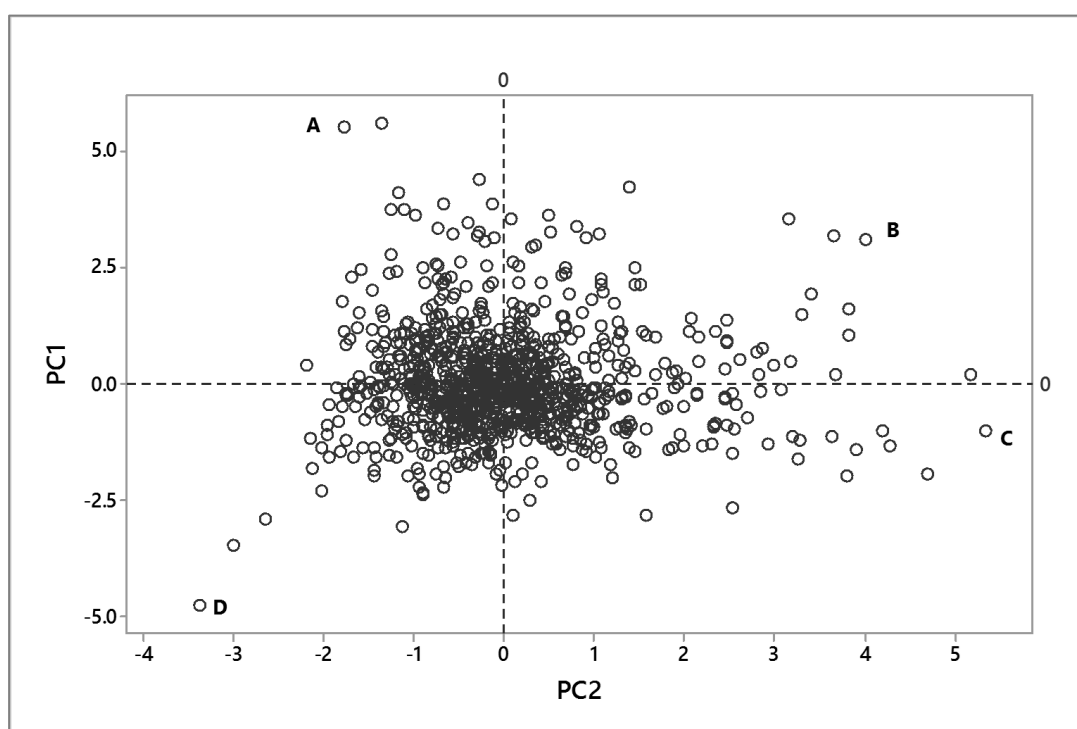
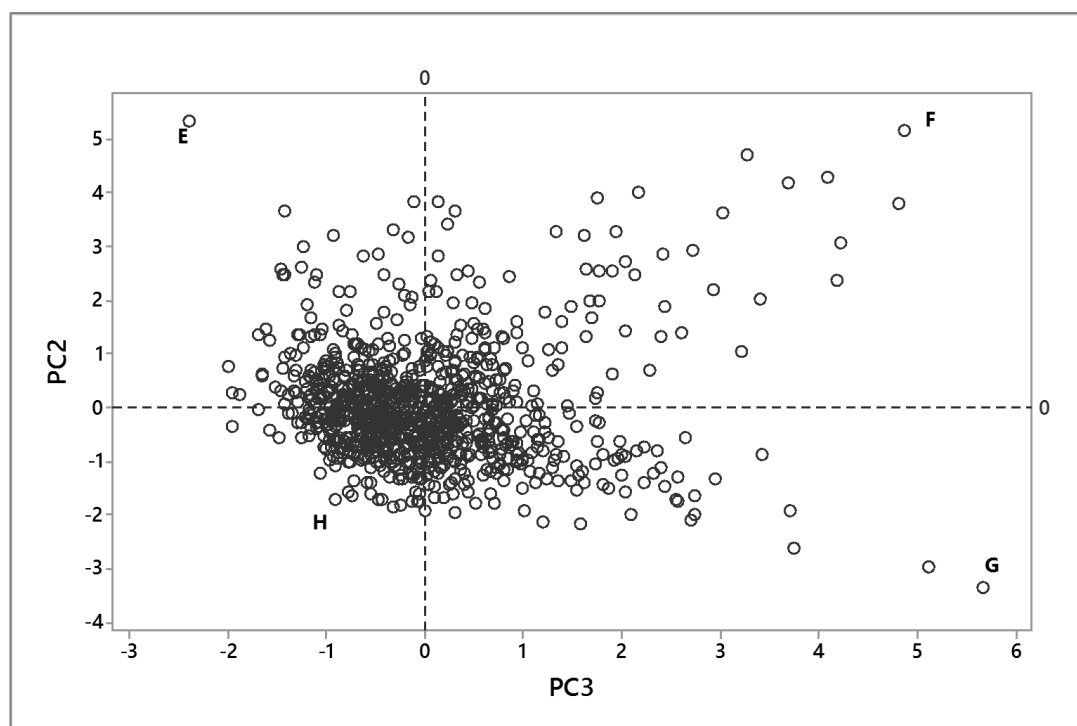


Figure 3.14 PC2 vs PC1 scores for the entire dataset of River Cuckmere

PC3 versus PC2 scores were compared in Figure 3.15. The end member E corresponded to the same record with point C in Figure 3.14 with a high nitrate concentration. Point F represented a high suspended solids concentration with a value of 240 mg/l. The end member G represented the same end member D in Figure 3.14. The last end member H was a low nitrate concentration record with a value of 0.2 mg/l.



*Figure 3.15 PC3 vs PC2 scores for the entire dataset of River Cuckmere*

### **3.4.3.3. Discussion**

The results of the principal component analysis on the entire dataset of River Cuckmere showed that PC1 was explaining 25.6% of the total variance and had strong influences on TRP concentration and conductivity, with a negative loading on BOD concentration and almost no loading on nitrate concentration. This suggests that PC1 might be representing a sewage effluent source. The end members in PC2 vs PC1 plot were conductivity, nitrate and BOD concentrations, whereas the end members in PC3 vs PC2 plot were nitrate, suspended solids and BOD concentrations. Presence of conductivity as an end member in the comparison plot with PC1 but not in the comparison of PC2 vs PC3 confirms that PC1 was urban based sewage effluent source. PC2 explained 22.3% of the total variance and had a quite high influence on nitrate concentration with also a high loading on suspended solids and

low loadings on conductivity and TRP concentration. Given that, PC2 seems to be an agriculture based diffuse source, yet having a low loading on TRP concentration makes it questionable PC3 explained 18.8% of the total variance and had a quite strong positive influence on BOD concentration with another strong loading on suspended solids concentration. PC3 loadings on nitrate and TRP concentrations were low and conductivity had a moderate loading. With this information, PC3 cannot be identified as either a diffuse source or a sewage source, since it had strong positive influence on BOD concentration, rather it could be related with groundwater source or storm water run-off.

### **3.4.4. River Otter**

#### ***3.4.4.1. Catchment Information***

The River Otter rises from the Blackdown Hills near the Devon and Somerset boundary in South West England. The river flows approximately 44 km and reaches the sea at Budleigh Salterton. River Tale is the largest tributary of the Otter and joins it in Ottery St Mary village. Other tributaries are River Wolf (confluence at north Honiton) and Wick Stream (confluence at south Honiton).

The Otter catchment area is considered to a considerable groundwater component to its flow. By this way, flows in Otter are relatively higher than in other catchments during dry summer periods. Catchment's geological structure is consisted of clay with flints overlaying greensand in the upper catchment area, whereas Triassic marl and sandstone is encountered below Honiton. A very high proportion of the catchment is rural and the land use for agricultural purposes is approximately 80%, mainly including farmlands with grazing pasture and a few arable fields (NRA, 1994; NRA, 1996).

#### ***3.4.4.2 Results***

Annual average TRP concentration time series of River Tern (Figure 3.16) indicated a large peak in year 1989 and that TRP concentration has been in decline since that year. For the flux time series, there were three peaks in years 1986, 1992 and 2010 due to extreme flowrates recorded in those years; 55.4 m<sup>3</sup>/s in January 1986, 39.7 m<sup>3</sup>/s in December 1992 and 23.7 m<sup>3</sup>/s in December 2010 while the

average flowrate for the overall study period was calculated to be 3.09 m<sup>3</sup>/s. Change point analysis indicated significant step changes; the year before change was 1992 with a probability of 0.9999 for TRP concentration and the year before change was recorded as 1993 with a probability of 0.9999 for TRP flux.

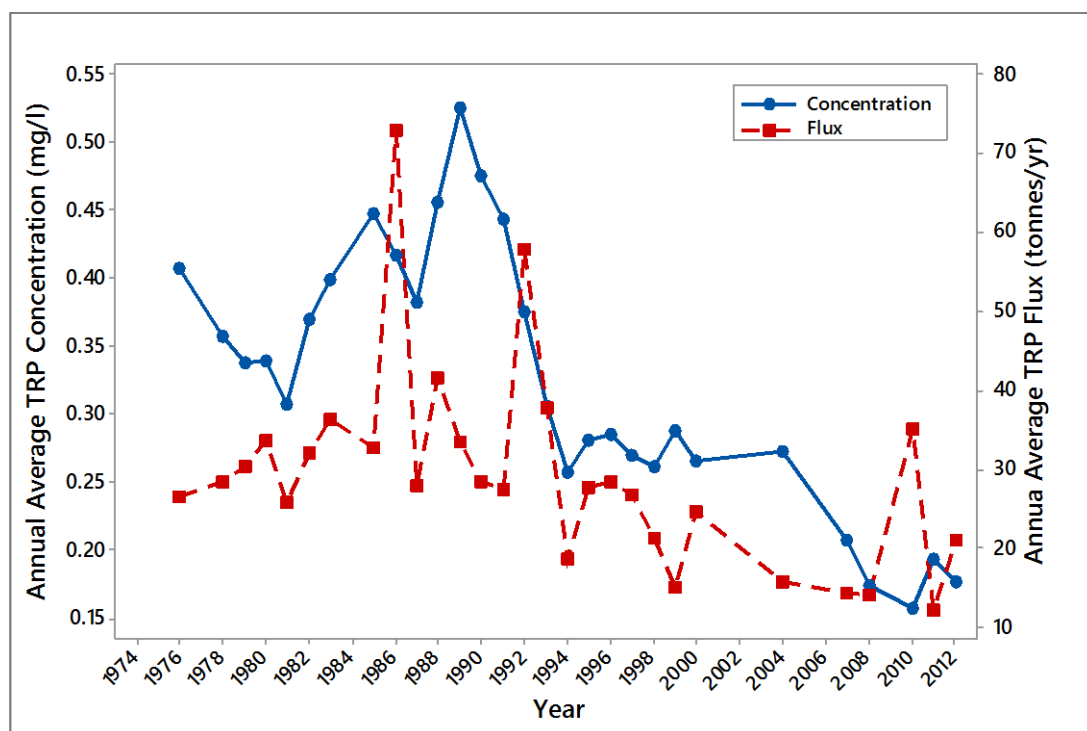


Figure 3.16 Annual average TRP Concentration and Flux time series of River Otter at Dotton Footbridge

#### 3.4.4.2.a. Principal Component Analysis

Four components with an eigenvalue >1 plus the first with an eigenvalue <1 were accepted for analysis and a cumulative variation of 85% was explained by these components (Table 3.8). PC1 had a strong negative loading on nitrate concentration and also a positive high loading on suspended solids concentration. For PC2, the highest loading was on suspended solids concentration with a negative sign and the

loadings on the other variables were almost equal. The third component had equally high negative loadings on BOD concentration and conductivity. PC4 had the highest loading on TRP concentration and also a relatively high negative loading on BOD concentration.

*Table 3.8 PCA results on River Otter, showing the principal components with eigenvalues > 1 and the first component coming after with an eigenvalue < 1.*

<b>Variable</b>	<b>PC1</b>	<b>PC2</b>	<b>PC3</b>	<b>PC4</b>
TRP Concentration	0.372	0.352	0.047	0.794
Suspended Solids Concentration	0.488	-0.771	-0.352	0.178
BOD Concentration	0.269	0.312	-0.664	-0.416
Nitrate Concentration	-0.695	-0.334	-0.250	0.276
Conductivity	-0.261	0.269	-0.609	0.298
<i>Eigenvalue</i>	1.2369	1.1788	1.0532	0.9427
<i>Cumulative variance explained (%)</i>	23.8	46.6	66.8	85.0

The scores of the first four principal components were plotted against one another and matrix plot is given (Figure 3.17). PC3 versus PC1 plot (Figure 3.18) and PC4 versus PC3 plot (Figure 3.19) were examined.

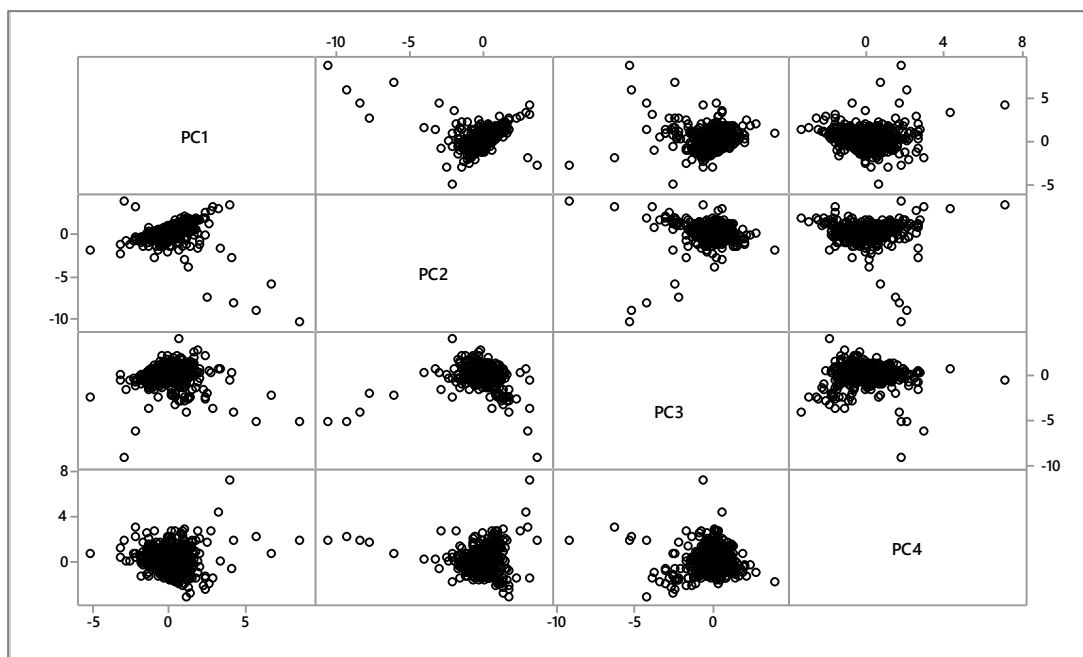
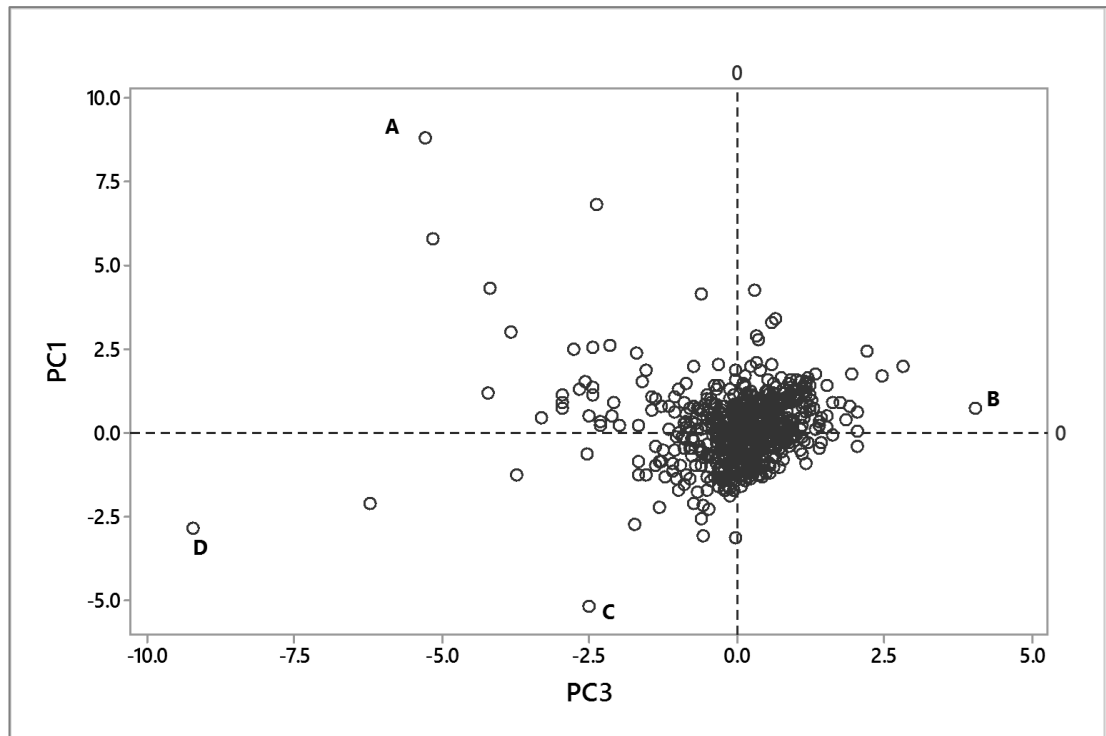


Figure 3.17 Matrix plot for comparisons of principal components on River Otter

The end member A in the PC3 vs PC1 plot represented the highest suspended solids concentration record in the whole dataset with a value of 982 mg/l. Point B corresponded to the lowest conductivity with 0  $\mu\text{S}/\text{cm}$  value. The end member C was the highest nitrate concentration with in the entire dataset with a value of 11.1 mg/l and similarly, the last end member D was the highest conductivity record with a value of 1050  $\mu\text{S}/\text{cm}$ .





*Figure 3.18 PC3 vs PC1 scores for the entire dataset of River Otter*

PC4 versus PC3 scores were compared in Figure 3.19. The end member E with the lowest conductivity value corresponded to the same record with the point B in Figure 3.18. Point F was the highest TRP concentration in the entire dataset with a value of 1.9 mg/l. The end member G with the highest suspended solids concentration was also represented by the end member D in Figure 3.18. The last end member H was a high BOD concentration record with a value of 8.8 mg/l.

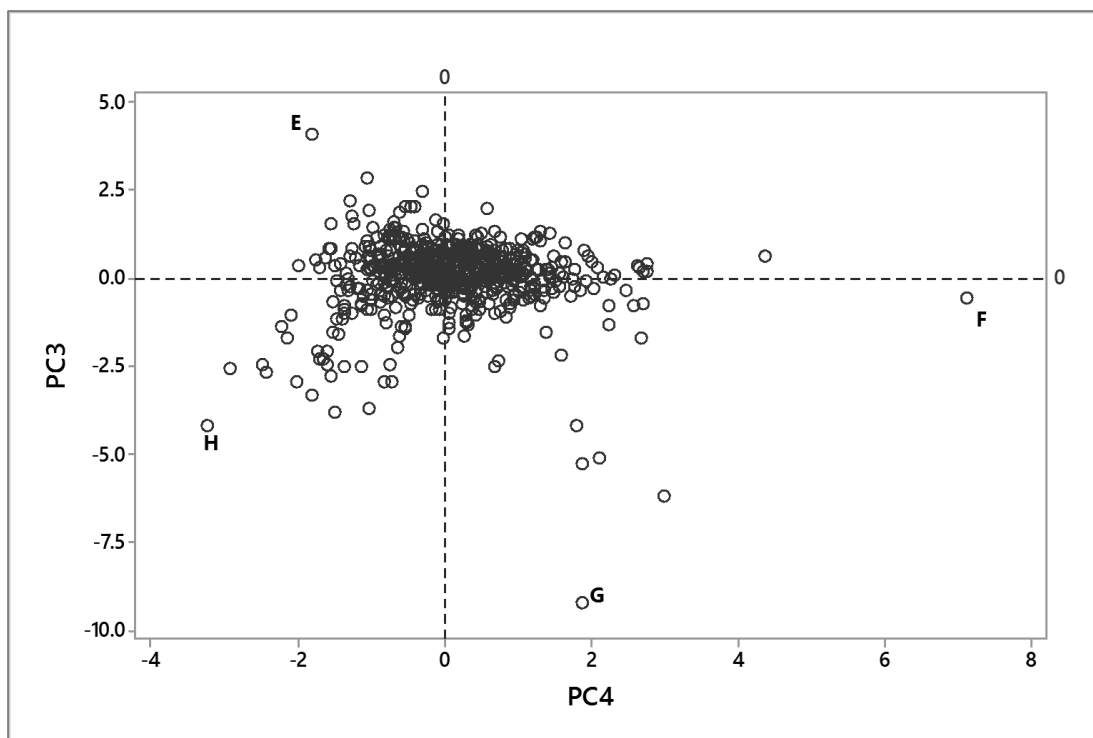


Figure 3.19 PC4 vs PC3 scores for the entire dataset of River Otter

#### 3.4.4.2.b. Principle Component Analysis Pre and Post Step Change

Principal component analysis was also performed regarding the step change; the data before and after the change point were analysed individually. All components with eigenvalue  $>1$  plus the first with an eigenvalue  $<1$  were accepted (the second with an eigenvalue  $<1$  was also accepted for the data of post step change since it had a quite close value to the one before); three principal components (PCs) defined according to this rule (Table 3.9). A cumulative variation of 69.6% for the data pre-change point and 78.3% variation for the post-change point data were explained by the PCs.

The first principal component before the step change data had high loadings on all components except BOD concentration. PC2 of the pre-change point data had

the highest loading on suspended solids concentration and almost equally high loadings on the other components, whereas PC3 had a quite strong loading on BOD concentration and almost no loading on conductivity. For the post-change point data, PC1 had high loadings on conductivity, TRP and BOD concentrations and PC2 had quite strong loadings on TRP and nitrate concentrations. PC3 had high loadings on conductivity, TRP and nitrate concentrations.

*Table 3.9 PCA results on River Otter – pre and post step change, showing the principal components with eigenvalues > 1 and the first component coming after with an eigenvalue <1*

<b>Variable</b>	<b><i>Pre step change</i></b>			<b><i>Post step change</i></b>		
	<b>PC1</b>	<b>PC2</b>	<b>PC3</b>	<b>PC1</b>	<b>PC2</b>	<b>PC3</b>
TRP Concentration	0.562	-0.372	-0.118	0.278	0.785	0.514
Suspended Solids Concentration	-0.333	-0.671	-0.245	0.582	-0.043	-0.045
BOD Concentration	-0.198	-0.358	0.898	0.550	0.025	-0.219
Nitrate Concentration	0.478	0.316	0.347	-0.297	0.616	-0.690
Conductivity	0.553	-0.428	-0.007	-0.439	0.054	0.458
<i>Eigenvalue</i>	1.4474	1.0532	0.9770	2.0800	0.9277	0.9081
<i>Cumulative variation explained (%)</i>	0.289	0.500	0.696	0.416	0.602	0.783

Comparisons of pre and post step change principle component scores were visualised with bar graphs for a better observation of the changes (Figure 3.20). It can be said that most of the components changed their signs and had considerable changes. One of these notable changes was the substantial decrease of the loading of

PC3 on BOD concentration after the step change. PC1 loadings on suspended solids and BOD concentrations increased after the step change. Also, after the step change, the strong negative loading of PC2 on suspended solids decreased and the loading on TRP concentration became quite important.

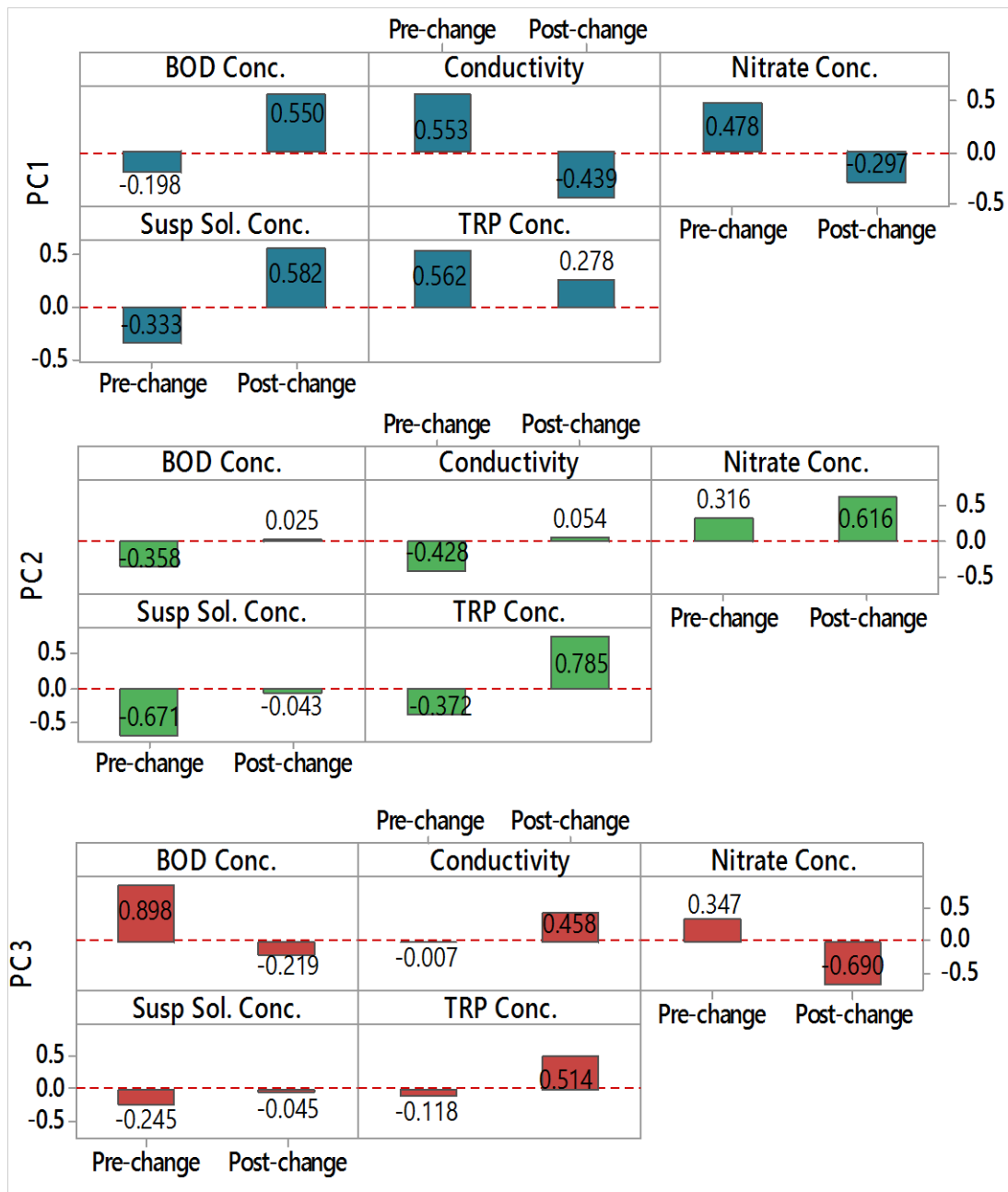
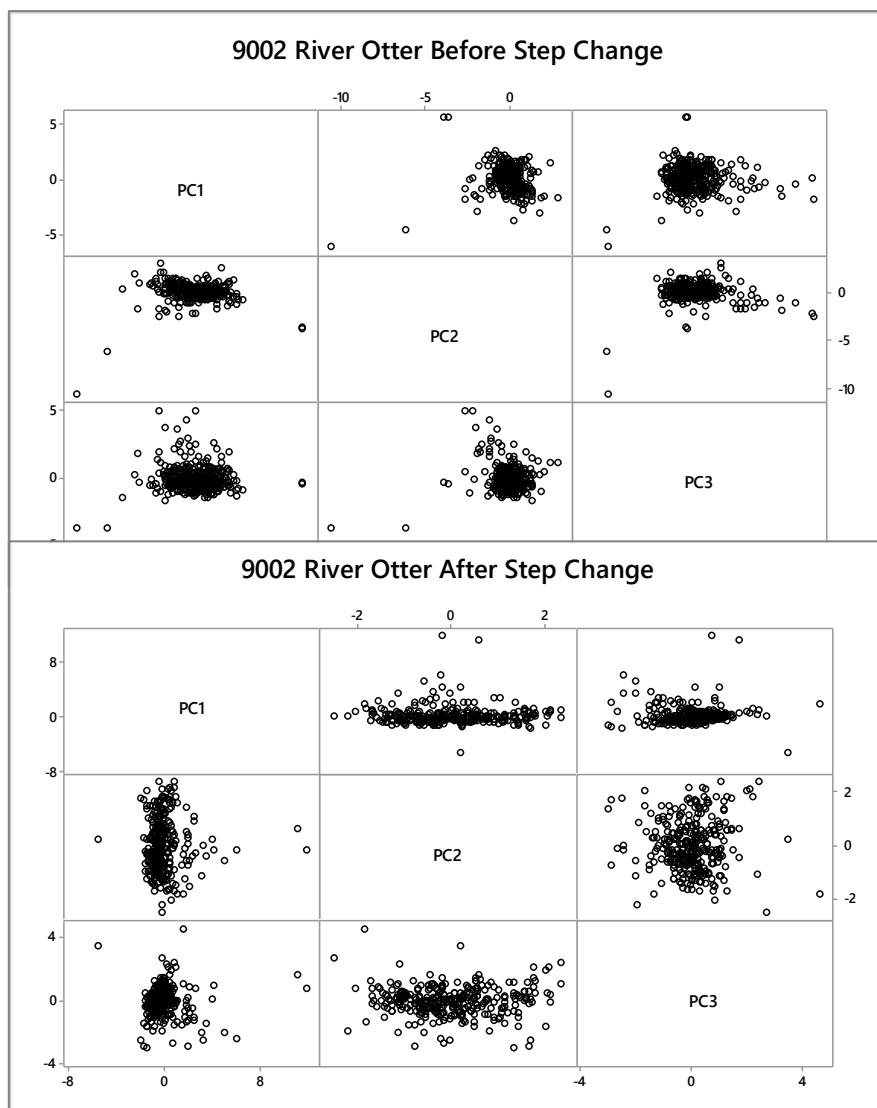


Figure 3.20 Comparisons of pre and post step change principal components for each variable on the data of River Otter

Matrix plots of the principal components are displayed (Figure 3.21). Comparisons for the pre and post step change principal components indicated distorted structures also accumulated trends parallel to PC2 after the step change.



*Figure 3.21 Matrix plot of principal components on the dataset of River Otter - pre and post step change*

Pre and post step change plots of PC2 versus PC1 were further compared (Figure 3.22). The end member A of the pre-step change scores represented a high suspended solids concentration with a value of 982 mg/l. Another end member B corresponded to a conductivity record of 920  $\mu\text{S}/\text{cm}$ , and end member C represented a low conductivity record of 122  $\mu\text{S}/\text{cm}$ . One of the end members of the post-change point scores was point D with a high suspended solids concentration of 810 mg/l.

Other end members of the post-change scores were point E with a low suspended solids concentration of 2.9 mg/l and point F with a low nitrate concentration value of 1.79 mg/l.

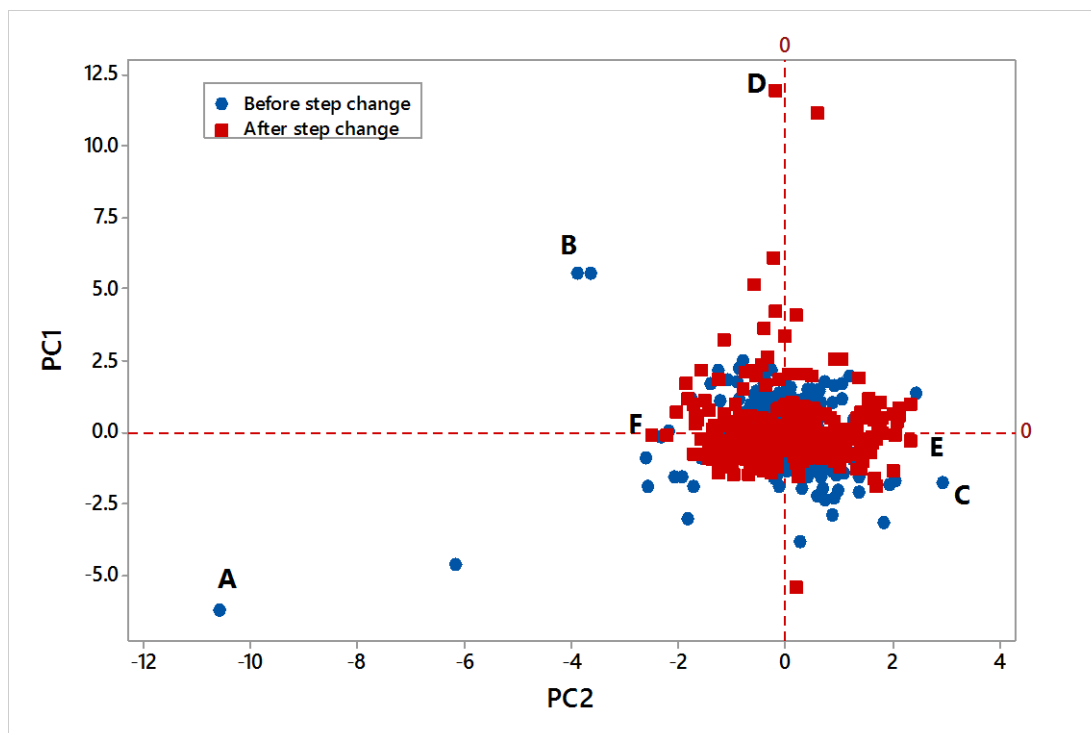


Figure 3.22 PC2 vs PC1 scores compared for the pre and post step change data of River Otter

#### 3.4.4.3. Discussion

Since Otter was highly related to its groundwater sources, it is quite difficult to make explicit and precise interpretations on the analysis results. Therefore, only the significant indicators in each principal component will be discussed. The first principle component explained 23.8% of the total variance and had a strong negative loading on nitrate concentration (Table 3.8) indicating that it was not an agricultural source. PC2 explained 22.8% of the total variance and had a quite strong negative

influence on suspended solids concentration. PC3 explained 20.2% of the total dataset variation and had negative loadings on all variables except for the quite low loading on TRP concentration. PC3 was strongly influenced by BOD concentration and conductivity were strongly influenced by PC3.. The fourth component explained 18.2% of the total variance and had a quite strong positive loading on TRP concentration. BOD concentration had also a high loading from PC4, yet it was a negative influence, thus it is difficult to correlate it with TRP concentration and describe a source contributor. If we were to consider only the loading on TRP concentration, we could define the PC4 as a highly contaminated agricultural run-off. Due to the catchment's strong interactions with its groundwater sources, the underlying source contributors have much complex relationships within, therefore a sophisticated approach in much more detail is required at this point.

#### ***3.4.4.3.a. The step change***

Examining the comparisons of pre and post step change principal component scores (Figure 3.10), one could say that most of the variables in all three principal components changed their sign after the step change. However, the sign of loadings in a PCA are fairly arbitrary and do not convey anything substantively important; what is more important is the absolute magnitude of the loadings. For, PC1, suspended solids and BOD concentrations had positive strong loadings after the step. The loading of PC2 on suspended solids concentration diminished after the step change, while TRP and nitrate concentration loadings became quite strong. The third principal component's strong positive loading on BOD concentration considerably decreased. Also, TRP concentration and conductivity had strong positive loadings



from PC3 while nitrate had a strong negative influence after the step change. The picture is again very complex and hard to interpret, but it can be said that the step change significantly affected all source contributors.

### **3.4.5. River Carnon**

#### ***3.4.5.1. Catchment Information***

The River Carnon is located in the west of Cornwall in south west, England. The catchment area is known for tin and copper mining activities and is a part of the Cornish Mining World Heritage Site. From the beginning of 18<sup>th</sup> century, the area was heavily mined for tin, copper, silver, lead and arsenic. The length of river with its tributaries has been impacted by these mining activities not just by one mine, but by multiple mines heavily draining a very large area (www.restorerivers.eu, 2015).

In 1991, a major pollution incident occurred on the catchment - an uncontrolled release of over 50 million liters of highly acidic metal laden from the abandoned mine Wheal Jane mine went into the River Carnon and then into the Fal Estuary. Following the incident, a series of controls and measures have been implemented by the Environment Agency for treatment of the mine water (NRA, 1994; Hunt & Howard, 1994).

#### ***3.4.5.2 Results***

River Carnon's annual average TRP concentration time series (Figure 3.23) displayed an oscillating profile with many peaks and the concentration had been increasing since mid-1980s until 2005 where it started to decline. In the flux time series, there was a large peak in year 2010 due an extreme flowrate recording of 59.07 m<sup>3</sup>/s in January 2010 while the average flowrate of the catchment for the overall study period was 1.02 m<sup>3</sup>/s. Change point analysis results were found to not

be statistically significant after familywise correction; the year before step in 2005 with a probability of 0.6970 and 1986 with a probability of 0.9083 for TRP concentration and flux, respectively.

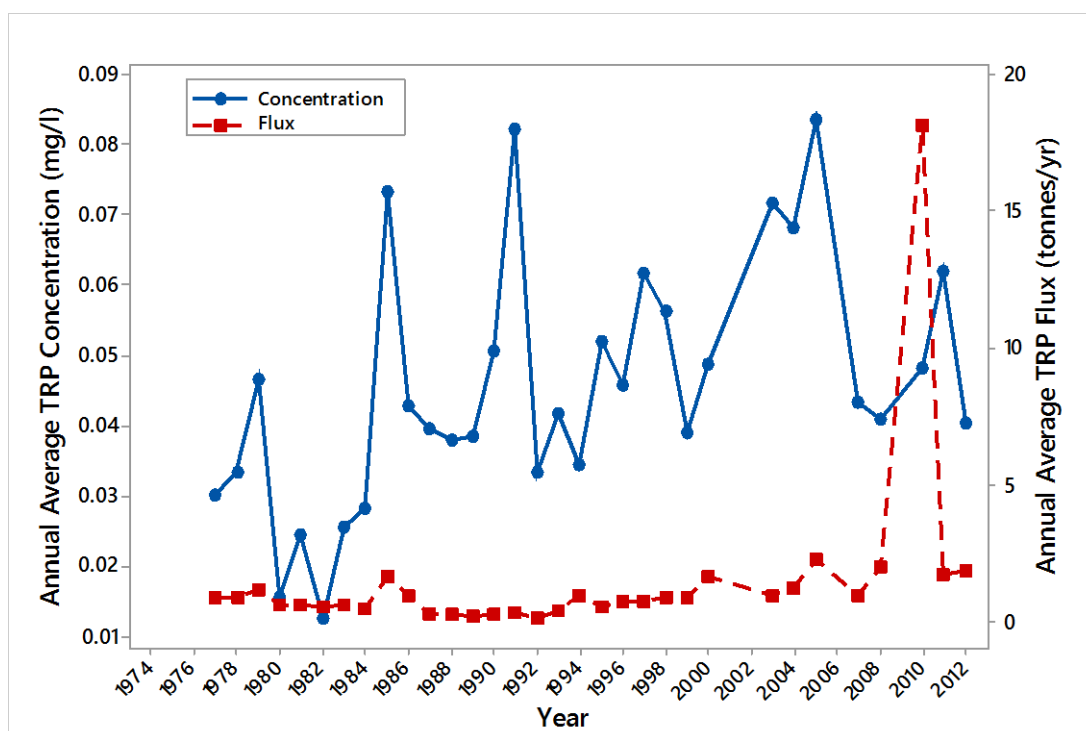


Figure 3.23 Annual average TRP Concentration and Flux time series of River Carnon at Devoran Bridge

#### 3.4.5.2.1. Principal Component Analysis

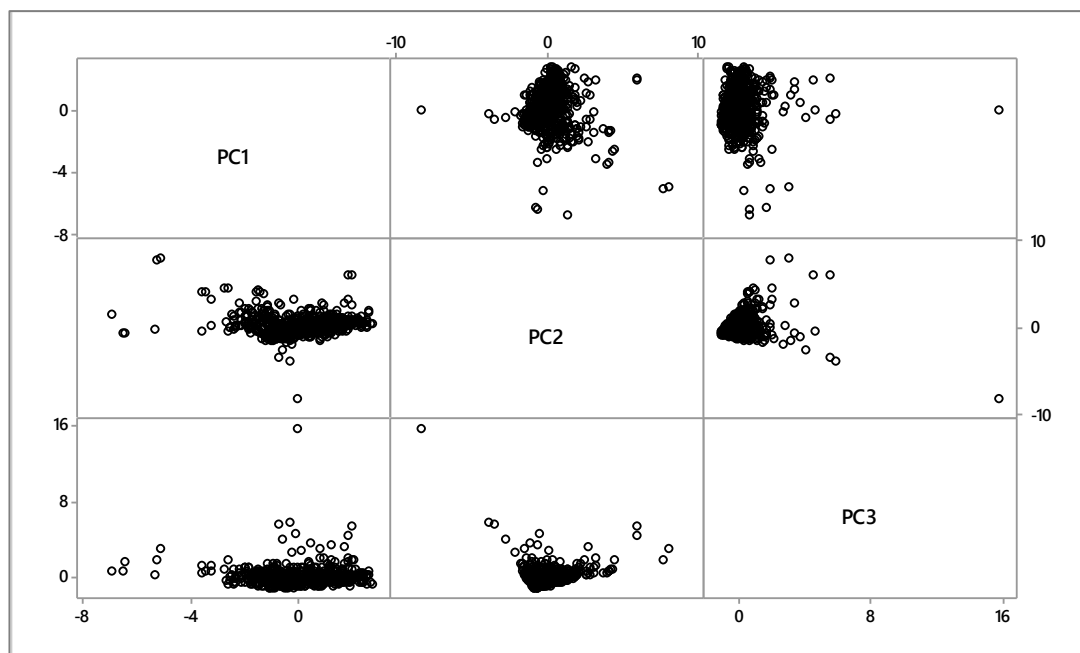
Three components with an eigenvalue  $>1$  plus the first with an eigenvalue  $<1$  were accepted for analysis and a cumulative variation of 69.6% was explained by these components (Table 3.10). PC1 had equally high loadings on TRP concentration and Conductivity, with also another high loading on Nitrate concentration and a high negative loading on suspended solids concentration. For the second component, the highest loading was on suspended solids concentration with a negative sign and

loadings for the rest of the variables were more or less similar. PC3 had a very high loading on BOD concentration with almost a negligible loading on conductivity.

*Table 3.10 PCA results on River Carnon, showing the principal components with eigenvalues > 1 and the first component coming after with an eigenvalue < 1.*

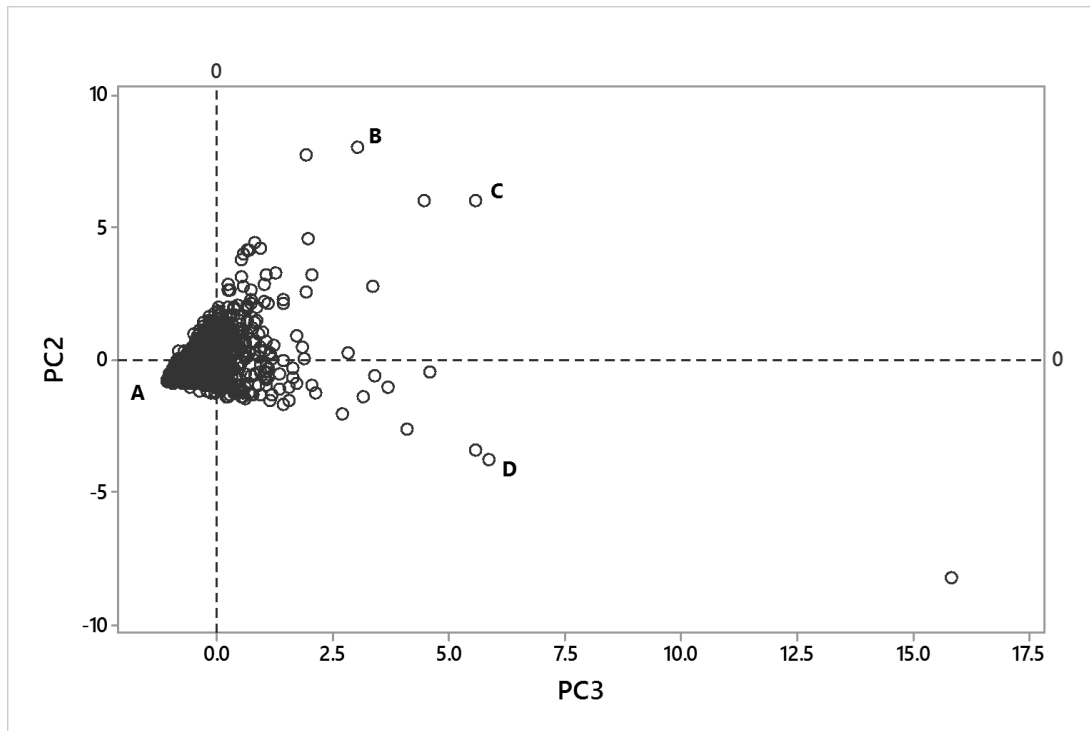
<b>Variable</b>	<b>PC1</b>	<b>PC2</b>	<b>PC3</b>
TRP Concentration	0.562	-0.372	-0.118
Suspended Solids Concentration	-0.333	-0.671	-0.245
BOD Concentration	-0.198	-0.358	0.898
Nitrate Concentration	0.478	0.316	0.347
Conductivity	0.553	-0.428	-0.007
<i>Eigenvalue</i>	1.4474	1.0532	0.9770
<i>Cumulative variance explained (%)</i>	28.9	50.0	69.6

The scores of the first three principal components were plotted against one another and matrix plot is given (Figure 3.24). PC3 versus PC2 plot (Figure 3.25) was further examined.



*Figure 3.24 Matrix plot for comparisons of principal components on River Carnon*

The point A in the PC3 vs PC2 plot represented a low conductivity record of 320  $\mu\text{S}/\text{cm}$ . The end member B corresponded to a high suspended solids concentration with a value of 399 mg/l. The end member C was a high BOD concentration record with a value of 17.9 mg/l and the last end member D was a high TRP concentration record with a value of 0.5 mg/l.



*Figure 3.25 PC3 vs PC2 scores for the entire dataset of River Carnon*

### **3.4.5.3. Discussion**

The first principal component explained a quite large portion of the dataset variation by 28.9% and had strong influences on TRP concentration, nitrate concentration and conductivity (Table 3.10). PC1 had a moderate negative loading on suspended solids concentration and small negative loading on BOD concentration. Considering the strong conductivity loading of PC1 and the mine water pollution incident in the catchment area (Hunt & Howard, 1994), PC1 might be representing a diffuse source of mine water run-off either combined with agricultural run-off or not. PC2 explained 21.1% of the total variation and had negative loadings on all variables except nitrate concentration. Despite the moderate positive nitrate loading, the strong negative loading on conductivity and negative loadings on other variables might suggest that PC2 could be representing a source of highly treated waste water

effluent. PC3 explained 19.6% of the total dataset variation with a quite strong positive loading on BOD concentration and almost no loading on conductivity. This kind of a source can be described as an improving contributor to catchment water quality, thus a not very contaminated source, such as a groundwater source could be representing the third principal component.





## **Chapter 4:**

### **Conclusions and Future Work**

#### **4.1. Introduction**

Since the implementation of Urban Waste Water Treatment Directive (UWWTD) and the subsequent Water Framework Directive (WFD), numerous actions have been undertaken to reduce direct phosphorus inputs into rivers from effluents of sewage treatment works. These actions included: installations of P-stripping units in sewage treatments works; and/or stringent concentration limits for P in the final sewage effluent. Since 1992 the UK has increased investments for the implementation of UWWTD and accordingly, considerable reductions of P concentrations in many rivers have been achieved. However, for an understanding of the results of these actions and the extent of P remediation that is required for a desired level of ecological recovery, a retrospective analysis on riverine phosphorus dynamics was needed.

The overall objective of this study was to investigate the evolution of riverine phosphorus at the national scale to comprehend the outcomes and effectiveness of the phosphorus remediation action. Therefore in Chapter 2, trend and change point analyses were performed on total reactive phosphorus (TRP) and total phosphorus

(TP) concentration and flux data over the period of 1974 - 2012. Datasets obtained from Harmonized Monitoring Scheme (HMS) were used with 230 HMS sites located in England, Wales and Scotland (no data were available from Northern Ireland).

Using the descriptive outcomes of Chapter 2, case examples representing various catchment characteristics were deducted and analysed in Chapter 3, for a better understanding of the underlying source contributors of riverine phosphorus levels. Therefore, Principal Component Analysis (PCA) method was employed to each site with an anticipation that a principal component that could be identified as an urban sewage effluent component would be present in each site and this would help us to track if the proposed step change was compatible with a step change that would present in that principal component. The PCA was carried out for each site using total reactive phosphorus (TRP), suspended solids, biological oxygen demand (BOD), nitrate and conductivity data.

## **4.2. Principle Findings**

### **4.2.1. Findings of Chapter 2**

- TRP and TP concentrations have been in decline since 1984 and 1985, for TRP and TP, respectively. Both TRP and TP fluxes peaked in 1985 and have been in decline since that year. This peak coincides with the peak in phosphate fertilizer usage of Great Britain in year 1984 followed by a declining profile

- TP flux has been declining at a higher rate than TRP flux. As TP represents all forms of phosphorus, it can be linked to the accumulated P serving as legacy phosphorus and this can explain why the TP flux has been declining parallel to the decline in fertilizer inputs
- A considerable sharp decrease was observed in both TRP and TP concentration main effects in the year 1994. The possible contributors to this decrease can be the decrease in fertilizer inputs for the year 1993 and/or increased water quality as a consequence of the implementation of UWWTD in 1991. Nevertheless, it should be noted that concentrations of TRP and TP started decrease in the mid-1980s, before the implementation of UWWTD.
- Most of the sites had declining trends for both TRP and TP concentrations and fluxes for the overall study period of 1974 – 2012
- The sites with larger declines in both TRP concentration and flux in the overall study period were from the Midlands, Wales and South East Regions of England, whereas South West England and Scotland have not seen large declines. For the last decade, the largest declines in TRP concentration were from the Midlands and South East regions
- Most of the sites showed significant decreases for both TRP and TP concentration in the last decade, but the number of sites having positive trends are higher than those having negative trends in TRP and TP fluxes. This was related to an increased average flow and the increased pressure on sewage treatment works due to population growth over the last decade
- Most of the records indicated significant step changes. The positions of most of the step changes are in downward trends in time series. For none of the

time series considered was there a step change before 1982. The modal year of any step change was 1997 for TRP concentration, but the modal year was delayed until 2000 for the TRP flux. For TP concentration and flux there was no step change before 1996 and the modal years were 2005 and 2004, respectively

- Step changes were rare for the rivers in Northern Scotland – an area of low population; extensive upland and livestock farming
- A comparison between the geometric means of the effect sizes of concentration and flux records indicated that the actual step change is in concentration data and variations in flow can restrict step changes calculated for the flux records, resulting in fewer change points and lower effect sizes than the concentration records
- Step changes were found to be important contributors to the overall decreasing trends
- The number of TP data available for analysis was much less than TRP data records. Due to the lack of TP records in the monitoring database, the number of sites having significant step changes for TP concentration and flux are quite low, therefore, it was difficult to make interpretations on the step changes of TP
- Most of the step changes in TRP concentration were encountered in the period of 1993 – 1997. Given that and the sharp decline in 1993 in TRP and TP concentration main effects, it was proposed that these steps were brought by the implementation of the UWWTD

#### **4.2.2. Findings of Chapter 3**

- The examples were chosen based on three parameters; trend type (negative, positive or no trend), step change (with or without a step change) and catchment type (rural or urban river). Out of 12 possible scenerios, only 5 sites were found to have suitable data; Principal Component Analysis was applied to the datasets of River Irwell, Tern, Cuckmere, Otter and Carnon.

##### ***4.2.2.1. River Irwell***

- River Irwell represented an urban catchment with a step change and a negative trend.
- The PCA results on the entire dataset indicated three principal components; PC1 and PC2 equally contribute to the total variation explaining approximately 25% variation each, and PC3 explaining 19% variation.
- The following interpretations were proposed for the principle components:
  - PC1 - a sewage effluent source
  - PC2 - a diffuse source such as agricultural run-off
  - PC3 (difficult to identify) – a groundwater or storm run-off source
- A comparison among the principal component analysis scores of the pre and post step change records showed that there was no impact of the step change on PC2, so it is not likely to be related to a sewage effluent source

- The greatest changes were on the loadings of PC1 on suspended solids and TRP concentration and the loadings of PC3 on BOD concentration and conductivity. These changes were interpreted as improvements in water quality after the step change; a result of the implementation of the UWWTD on a river with a highly urban character.

#### **4.2.2.2. River Tern**

- River Tern represented a rural catchment with no step change and a negative trend.
- Four principal components were defined. PC1 explained 26%, PC2 explained 21.4%, PC3 explained 20.7% and PC4 explained 16% of the total dataset variation.
- PCs were difficult to interpret; the following estimations were made for the identities of PCs;
  - PC1 - a diffuse source with agricultural run-off
  - PC2 – a sewage source
  - PC3 – a groundwater source
  - PC4 (difficult to identify) – an industrial effluent source i.e. effluents from dairy production plants
- The dominant end members in catchment chemistry were nitrate and suspended solids, which was expected from a highly rural catchment.

#### **4.2.2.3. River Cuckmere**

- River Cuckmere represented a rural catchment with no step change and a positive trend.
- Three principal components were defined. PC1 explained 25.6%, PC2 explained 22.3% and PC3 explained 18.8% of the total dataset variation.
- PCs were proposed to be representing the following:
  - PC1 – a sewage effluent source
  - PC2 (difficult to interpret) – an agriculture based diffuse source
  - PC3 - a groundwater source or storm water run-off

#### **4.2.2.4. River Otter**

- River Otter represented a rural catchment with a step change and a negative trend.
- Four principal components were defined for the entire dataset. PC1 explained 23.8%, PC2 explained 22.8%, PC3 explained 20.2% and PC4 explained 18.2% of the total dataset variation.
- Due to the catchment's strong interactions with its groundwater sources, it was quite difficult to make explicit interpretations on the analysis results, therefore, no estimation could be made for the components.
- A much more detailed analysis is required at to identify the source contributors.

#### **4.2.2.5. River Carnon**

- River Carnon represented an urban catchment with no step change and a positive trend.
- Three principal components were defined. PC1 explained 28.9%, PC2 explained 21.1% and PC3 explained 19.6% of the total dataset variation.
- The following interpretations were made for the principle components:
  - PC1 - a diffuse source of mine water run-off either combined with agricultural run-off or not.
  - PC2 - a source of highly treated waste water effluent
  - PC3 – a groundwater source

#### **4.2.3. Limitations of the Datasets and Techniques**

As an overall outcome of Chapter 2, it was proposed that the step changes in riverine P concentration and flux time series were brought about by the implementation of the Urban Waste Water Treatment Directive (UWWTD). To validate this hypothesis, firstly the individual records of the discharges from sewage treatment works were reviewed, however for most of the sites, there weren't sufficient phosphorus data. As an alternative approach, Principal component analysis (PCA) was conducted to be able to track down the urban source contributor i.e. to see whether the corresponding step change could also be observed within the principle component. However, in none of the case examples was there an explicit principle component that could be construed with an urban or any other source contributor. The reason for the difficulty on identification of the principle



components was probably due to the complexity of the urban sources, i.e. there were more than one sewage treatment work (STW) affecting each catchment, and each of these STWs had consent changes in different time periods. Therefore, the PCA technique turned out not to be an appropriate technique to analyse this type of datasets.

#### **4.3. Recommendations for Future Work**

Further work could be carried out by conducting PCA on other case examples. However, size selection specifications should be narrowed down to be able perform a healthier analysis. The ideal examples would be the sites from small catchments near small population areas with only one sewage treatment work affecting the catchment and also having suitable datasets for analyses. To find this sort of example sites needs a detailed inventory of all the sites.

Another approach to further work could be to study a large urban river such as; Thames, Severn, Ouse, Stour etc. in which the data records are much more consistent and the records for phosphorus discharges from STWs are available. The changes in the P discharge records from the STWs would allow us to see whether the step change in the P records of the river corresponded to any consent change in the STWs. However, this would require a much more detailed analysis since there are many tributaries and multiple monitoring sites of the large rivers along with multiple STWs discharging into those catchments.

Analysis could also be performed with sewage tracers, such as boron which has been extensively used in detergents. However, one should keep in mind that the use of boron in detergents has halved over the last 10-20 years therefore, there could be some inconsistency between the earlier records and the recent ones. Also, a limitation could arise with the lack of records for some sites.

Further work can also be conducted on the effects of changes in agricultural policies/methods, crops, and land use etc. with a catchment based approach and/or at national scale.

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## Appendices

### Appendix 1

#### Correction of Familywise Error in Change Point Analysis

*Table A1.1 New significance levels to correct familywise error in change point analysis*

No. of tests	Actual significance level to use
1	0.95
2	0.974679434
3	0.983047572
4	0.987258545
5	0.989793782
6	0.991487555
7	0.992699168
8	0.993608849
9	0.994316955
10	0.994883803
11	0.995347828
12	0.995734681
13	0.996062136
14	0.996342897
15	0.996586287
16	0.996799302
17	0.996987295
18	0.997154429
19	0.997303994
20	0.997438621
21	0.997560443
22	0.997671202
23	0.997772342
24	0.997865062
25	0.997950372
26	0.998029126
27	0.998102052
28	0.998169774
29	0.998232829
30	0.998291684
31	0.998346746
32	0.998398369
33	0.998446865
34	0.998492511
35	0.998535551

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36	0.998576201
37	0.998614655
38	0.998651087
39	0.998685652

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## Appendix 2

### Summary of Results for All Sites

*Tablo A2.1 Summary of TRP concentration results for all sites*

HMS SiteID	Region ID	Name of River	Length of time series	Year before change	Probability of step change	Change point valid after familywise correction	Effect size of the step change	Actual size of the step change	Type of Trend
1001	NW	Mersey	35	1997	0.999929	YES	0.747	0.313963245	Negative
1002	NW	Mersey	33	1999	0.999746	YES	0.833	0.299866955	Negative
1003	NW	Irwell	35	1997	0.999899	YES	0.777	0.392271479	Negative
1004	NW	Tame	33	2001	0.996541	NO	0.671	0.315545712	Negative
1005	NW	Weaver	28	2000	0.989930	NO	0.964	0.173262271	Positive
1006	NW	Alt	28	1991	0.999983	YES	0.852	0.526611388	Negative
1007	NW	Ribble	32	1997	0.999233	YES	0.585	0.366560248	Negative
1008	NW	Ribble	31	1999	0.94775484	NO	0.505	0.183939982	Positive
1009	NW	Calder	32	1997	0.980589	NO	0.767	0.212325153	Positive
1010	NW	Wyre	22	1990	0.995437	NO	0.914	0.184297773	Negative
1012	NW	Kent	24	1989	0.999891	YES	0.952	0.688441455	Negative
1014	NW	Leven	26	1996	0.999754	YES	0.515	0.716641111	Negative
1015	NW	Douglas	28	1996	0.958959	NO	0.606	0.384743014	Positive
1016	NW	Darwen	30	1999	0.965272	NO	0.969	0.129638535	Positive
1017	NW	Eden	25	1989	0.999930	YES	0.974	0.648058588	Negative
1018	NW	Eamont	23	1990	0.999840	YES	0.676	0.645667217	Negative
1019	NW	Eden	21	1989	0.980898	NO	0.833	0.012137554	Positive
1020	NW	Esk	21	1988	0.997668	YES	0.818	0.30367965	Negative
1021	NW	Lyne	17	1988	0.981957	NO	-	0.293733029	Negative
1022	NW	Derwent	25	1996	0.999280	YES	0.818	0.627572158	Negative
1023	NW	Lune	25	1988	0.991038	NO	0.757	0.21211284	No
1024	NW	Beela	9	2005	0.909282047	NO	0.79	0.191016368	Positive
1025	NW	Eden	6	2006	0.967567	NO	0.919	0.470482094	Negative
2001	NE	Tweed	20	2003	0.999559	YES	0.813	0.552057971	Negative
2009	NE	Coquet	18	1998	0.983722	NO	0.944	0.427045598	Negative
2012	NE	Wansbeck	20	2002	0.999210	YES	0.696	0.613396171	Negative
2020	NE	North Tyne	18	2002	0.966385	NO	0.631	0.259670159	Negative
2021	NE	South Tyne	22	2004	0.988476	NO	0.974	0.496902426	No
2026	NE	Derwent	18	2004	0.996410	NO	0.792	0.615659903	Negative
2044	NE	Wear	21	1996	0.999040	YES	0.681	0.478628135	Negative
2058	NE	Tees	20	1986	0.993526	NO	0.494	0.01479886	Positive
2061	NE	Tees	15	2003	0.939291203	NO	0.953	0.334711758	Positive

2923	NE	Tyne	21	1992	0.998585	YES	0.904	0.362560641	Negative
3006	MI	Trent	30	1997	0.999973	YES	0.946	0.467407269	Negative
3007	MI	Trent	35	1997	0.999997	YES	0.898	0.437346122	Negative
3008	MI	Trent	29	1997	0.999755	YES	0.942	0.361281038	Negative
3009	MI	Idle	27	1998	0.999934	YES	0.929	0.588927254	Negative
3010	MI	Soar	23	1997	0.999905	YES	0.911	0.511748921	Negative
3011	MI	Derwent	28	1996	0.999868	YES	0.984	0.665554669	Negative
3012	MI	Stour	28	1999	0.999964	YES	-	0.412470444	Negative
3013	MI	Tame	25	1996	0.999860	YES	-	0.418211388	Negative
3014	MI	Sowe	26	1997	0.999925	YES	0.954	0.478255631	Negative
3015	MI	Dove	25	1996	0.999657	YES	0.782	0.422258857	Negative
3019	MI	Tern	26	1998	0.991206	NO	0.757	0.216164293	Negative
3029	MI	Teme	27	1995	0.999350	YES	0.878	0.313154785	Negative
3227	MI	Severn	28	1996	0.999418	YES	0.964	0.466301441	Negative
3416	MI	Avon	29	1997	0.999988	YES	0.87	0.724973677	Negative
3752	MI	Severn	26	1995	0.999665	YES	-	0.372462235	Negative
4001	NE	Hull	19	2000	0.999710	YES	-	0.675651513	Negative
4003	NE	Ouse	18	1999	0.999627	YES	0.934	0.485526554	Negative
4004	NE	Aire	18	1997	0.999126	YES	0.707	0.474979206	Negative
4005	NE	Aire	13	2005	0.994114	NO	0.777	0.399961166	Negative
4006	NE	Calder	4	1997	0.698805788	NO	0.666	0.563231878	Negative
4007	NE	Don	13	2000	0.985918	NO	0.353	0.313831738	Negative
4008	NE	Don	17	2000	0.756568115	NO	0.909	0.197430001	Positive
4009	NE	Dearne	14	1999	0.995988	NO	0.934	0.237713553	Negative
4010	NE	Rother	13	2000	0.996309	YES	-	0.285277774	Negative
4012	NE	Esk	11	2004	0.991578	NO	0.828	0.505809913	Negative
4013	NE	Wharfe	18	2005	0.998046	YES	-	0.364888148	Negative
4014	NE	Derwent	12	2004	0.996496	YES	0.989	0.603319119	Negative
4015	NE	Ouse	16	2003	0.999213	YES	0.848	0.478286653	Negative
5400	AN	Ancholme	1	2012	0.950213	NO			
5410	AN	Witham	7	2006	0.924734596	NO	0.841	0.58580911	Negative
5501	AN	Welland	8	2003	0.965782	NO	0.919	0.485103732	Negative
5502	AN	Welland	15	2003	0.998916	YES	-	0.588549793	Negative
5510	AN	Nene	16	1982	0.998836	YES	0.979	0.755156699	Negative
5511	AN	Nene	13	2006	0.997099	YES	-	0.715997815	Negative
5626	AN	Bedford Ouse	16	1984	0.999213	YES	0.888	0.691544849	Negative
5651	AN	Ely Ouse	11	1984	0.950826	NO	-	0.469254089	Negative
5683	AN	Mid Lev Main Dr	6	1982	0.967567	NO	0.791	0.688741853	Negative
5714	AN	Wensum	17	1986	0.999483	YES	-	0.632498472	Negative
5722	AN	Bure	17	1986	0.999483	YES	0.924	0.788141228	Negative
5810	AN	Stour	18	2002	0.998787	YES	0.932	0.589983148	Negative
5811	AN	Stour	18	1987	0.999126	YES	0.979	0.704047703	Negative

5820	AN	Colne	17	1985	0.999483	YES	0.909	0.523887354	Negative
5830	AN	Blackwater	13	1985	0.994114	NO	-	0.697136946	Negative
5840	AN	Chelmer	17	1985	0.999483	YES	-	0.695814459	Negative
6001	SE	Thames	21	1997	0.999883	YES	0.994	0.703013705	Negative
6002	SE	Cherwell	16	2000	0.993010	NO	-	0.647974468	Negative
6003	SE	Thame	17	1997	0.998928	YES	-	0.648198991	Negative
6004	SE	Kennett	25	1997	0.999921	YES	0.848	0.779646298	Negative
6005	SE	Loddon	14	1986	0.986678	NO	0.974	0.413784878	Negative
6006	SE	Thames	17	1988	0.999378	YES	-	0.760010657	Negative
6007	SE	Colne	17	1997	0.999483	YES	-	0.796583893	Negative
6008	SE	Wey	16	1997	0.999213	YES	0.904	0.631229718	Negative
6009	SE	Mole	16	1999	0.998836	YES	0.863	0.842804735	Negative
6010	SE	Thames	30	1995	0.999986	YES	0.969	0.573553129	Negative
6101	SE	Lee	23	2000	0.999945	YES	-	0.729755971	Negative
6102	SE	Lee	15	2000	0.998916	YES	-	0.768042987	Negative
6104	SE	Lee	12	2000	0.996496	YES	0.989	0.571984501	Negative
6105	SE	Lee	15	1998	0.998660	YES	0.982	0.413823331	Negative
6106	SE	Roding	18	1999	0.999375	YES	0.848	0.60291875	Negative
7001	SE	Medway	32	1997	0.999985	YES	0.803	0.337149992	Negative
7002	SE	Eden	27	1999	0.998772	YES	0.986	0.214796566	Negative
7003	SE	Great Stour	25	1997	0.999930	YES	0.767	0.516764703	Negative
7004	SE	Rother	16	2005	0.999041	YES	0.368	0.482717702	Negative
7005	SE	Cuckmere	28	2000	0.988436	NO	0.982	0.268005104	Positive
7006	SE	Ouse	23	1997	0.999840	YES	0.904	0.418007214	Negative
7007	SE	Rother	29	1999	0.999933	YES	0.883	0.270858626	Negative
7008	SE	Arun	25	1997	0.999416	YES	0.956	0.499850657	Negative
7011	SE	Blackwater	20	1999	0.999315	YES	-	0.386078378	Negative
7012	SE	Test	23	1999	0.999945	YES	0.976	0.632990514	Negative
7013	SE	Itchen	22	2000	0.999832	YES	0.843	0.584177505	Negative
8001	SW	Avon	21	1995	0.997366	NO	-	0.411966504	Negative
8002	SW	Somerset Frome	15	1990	0.997974	YES	0.962	0.516556489	Negative
8003	SW	Midford Brook	22	1992	0.999808	YES	0.994	0.507144952	Negative
8004	SW	Avon	23	1997	0.999892	YES	0.777	0.52218265	Negative
8100	SW	Avon	18	1998	0.999627	YES	0.575	0.593115374	Negative
8200	SW	Stour	8	1998	0.870187823	NO	-	0.680804701	Positive
8201	SW	Stour	11	2005	0.938786555	NO	0.792	0.081451325	Positive
8300	SW	Piddle	15	2004	0.993537	NO	0.595	0.224629153	Negative
8326	SW	Tone	10	1991	0.829201833	NO	0.888	0.022159915	Positive
8400	SW	Frome	18	1998	0.999627	YES	0.929	0.4512981	Negative
8426	SW	Parrett	19	2005	0.998145	YES	0.893	0.316063831	Negative
9001	SW	Axe	26	1998	0.996134	NO	0.994	0.429804894	Negative
9002	SW	Otter	29	1992	0.999994	YES	0.808	0.39642225	Negative

9003	SW	Exe	18	1996	0.998046	YES	0.626	0.299736859	Negative
9008	SW	Teign	21	1996	0.982708	NO	0.981	0.146935186	Negative
9011	SW	Dart	21	1993	0.999159	YES	0.969	0.408880952	Negative
9013	SW	Avon	18	1996	0.998969	YES	0.914	0.520288426	Negative
9014	SW	Plym	29	1995	0.999933	YES	0.924	0.332775139	Negative
9015	SW	Tavy	21	1996	0.999719	YES	0.993	0.460200373	Negative
9017	SW	Tamar	32	1991	0.999995	YES	0.929	0.297348948	Negative
9023	SW	Lynher	19	2003	0.996257	NO	0.914	0.335570646	Negative
9024	SW	Fowey	19	1996	0.997532	YES	0.767	0.168940032	Negative
9025	SW	Fal	32	1993	0.999970	YES	0.525	0.317066965	Negative
9026	SW	Carnon	32	2005	0.696960478	NO	0.939	0.041506475	Positive
9027	SW	Camel	22	1997	0.997656	NO	0.964	0.369479559	Negative
9028	SW	Torridge	19	1992	0.999244	YES	0.979	0.376472674	Negative
9030	SW	Taw	21	1996	0.999509	YES	0.863	0.41448105	Negative
9031	SW	Taw	9	2003	0.972268	NO	-	0.520117553	Negative
9035	SW	Yeo	20	1989	0.999488	YES	0.914	0.345460102	Negative
9036	SW	Exe	21	1986	0.998906	YES	0.792	0.331935266	Negative
9037	SW	Red	26	1993	0.999589	YES	0.838	0.351911745	Negative
10001	WA	Dee	16	1995	0.930686643	NO	0.707	0.641991965	Negative
10002	WA	Dee	27	1996	0.999815	YES	-	0.541001929	Negative
10003	NW	Dee	23	1999	0.999877	YES	0.934	0.444530239	Negative
10004	WA	Alwen	28	1987	0.999787	YES	-	0.737020262	Negative
10005	WA	Clywedog	27	1988	0.999966	YES	0.803	0.959926327	Negative
10006	WA	Alyn	22	1999	0.997656	NO	0.892	0.2680106	Negative
10007	WA	Clwyd	25	1997	0.999618	YES	0.666	0.315260051	Negative
10008	WA	Elwy	24	1998	0.997758	NO	-	0.274632609	Negative
10009	WA	Ogmore	30	1997	0.999992	YES	-	0.732378139	Negative
10010	WA	Neath	25	1995	0.999974	YES	0.929	0.693916732	Negative
10011	WA	Ely	27	1997	0.999934	YES	0.994	0.488283593	Negative
10012	WA	Taff	23	1997	0.999917	YES	0.949	0.793639629	Negative
10013	WA	Rhymney	20	1998	0.999488	YES	-	0.627807385	Negative
10014	WA	Dwyrdd	18	1997	0.997341	YES	0.954	0.386316742	Negative
10015	WA	Dysynni	27	1992	0.999900	YES	0.969	0.541382344	Negative
10016	WA	Gwyrffai	28	1995	0.999968	YES	0.979	0.570349636	Negative
10017	WA	Dovey (Or Dyfi)	27	1992	0.999877	YES	0.838	0.646792533	Negative
10018	WA	Wnion	17	1996	0.892792312	NO	0.707	0.442832566	Positive
10019	WA	Mawddach	19	1996	0.799885238	NO	0.818	0.337166685	Positive
10020	WA	Glaslyn	20	1995	0.975347	NO	-	0.442059069	Positive
10021	WA	Dwyfawr	17	1995	0.973139	NO	0.851	0.661257262	Negative
10022	WA	Ogwen	18	1998	0.987415	NO	0.972	0.314223306	Negative
10023	WA	Conwy	29	1994	0.999950	YES	0.974	0.627293417	Negative
10024	WA	Tawe	26	1998	0.999966	YES	0.919	0.663525703	Negative

10025	WA	Loughor	19	2002	0.999598	YES	0.621	0.654740292	Negative
10026	WA	Towy (Or Tywi)	23	1990	0.974261	NO	0.989	0.556081051	Negative
10027	WA	Taf	26	1994	0.999973	YES	0.686	0.70767627	Negative
10028	WA	Eastern Cleddau	15	1990	0.992250	NO	0.772	0.522202274	Negative
10030	WA	Teifi	14	1999	0.992553	NO	0.09	0.275233032	Negative
10032	WA	Rheidol	21	2006	0.664089019	NO	0.929	0.437691476	Positive
10033	WA	Usk	22	1992	0.999808	YES	0.641	0.427953016	Negative
10034	WA	Afon Lwyd	20	1994	0.982009	NO	0.742	0.141433126	Negative
10035	WA	Ebbw Fawr	16	1997	0.994084	NO	0.606	0.605619174	Negative
10036	MI	Wye	18	1985	0.992651	NO	-	0.491269044	Negative
10037	WA	Wye	31	1995	0.999997	YES	0.898	0.556282432	Negative
10038	WA	Elan	17	1992	0.995878	NO	0.828	0.527583311	Negative
10039	WA	Western Cleddau	24	1990	0.998660	YES	0.838	0.23733795	Negative
10040	WA	Gwili	21	1995	0.988531	NO	0.404	0.492525521	Negative
10041	WA	Ystwyth	17	2007	0.869267506	NO	0.616	0.103402947	Negative
10042	WA	Nant Y Fendrod	16	2008	0.912137773	NO	0.479	0.002838699	Positive
11001	SEPA N	Wick	26	1991	0.588887709	NO	0.191	0.518530593	Positive
11002	SEPA N	Shin	25	1993	0.659274095	NO	0.616	0.049355259	Positive
11003	SEPA N	Conon	26	1985	0.951664	NO	0.444	0.343306108	Negative
11004	SEPA N	Beauly	22	1993	0.846830897	NO	0.661	0.118852191	No
11005	SEPA N	Ness	29	1993	0.963531	NO	0.792	0.321809195	Negative
11006	SEPA N	Nairn	31	1988	0.996199	NO	0.686	0.507138438	Negative
11007	SEPA N	Findhorn	31	1986	0.978163	NO	0.146	0.451702404	Negative
11008	SEPA N	Lochy	24	1990	0.347318924	NO	0.247	1.038968736	Positive
11009	SEPA N	Carron	25	1993	0.779612789	NO	0.166	0.295741583	Positive
11010	SEPA N	Thurso	26	1988	0.501222415	NO	0.373	1.030822241	Positive
12001	SEPA N	Lossie	12	1998	0.513809057	NO	0.282	0.206433215	Negative
12002	SEPA N	Spey	17	2006	0.810906422	NO	0.868	0.053686413	Positive
12003	SEPA N	Deveron	9	1993	0.931029339	NO	0.676	0.174463473	Negative
12004	SEPA N	Ugie	15	1997	0.978506	NO	0.808	0.125551377	Negative
12005	SEPA N	Ythan	18	1991	0.990346	NO	0.484	0.298040674	Negative
12006	SEPA N	Don	13	1995	0.897954149	NO	0.914	0.163281341	Positive
12007	SEPA N	Dee	12	1981	0.962449	NO	0.902	0.503288079	Negative
13001	SEPA E	Eden	25	2000	0.998680	YES	-	0.433380824	Negative
13002	SEPA E	Earn	21	2000	0.999573	YES	-	0.644027454	Negative
13003	SEPA E	Tay	28	2000	0.999964	YES	-	0.706259788	Negative
13004	SEPA E	Dighty Water	21	2000	0.999864	YES	0.915	0.705335691	Negative
13005	SEPA E	South Esk	23	1999	0.999700	YES	-	0.619543673	Negative
13006	SEPA E	North Esk	23	2000	0.999892	YES	0.818	0.594442477	Negative
14001	SEPA E	Leven	17	1997	0.994359	NO	0.757	0.395535799	Negative
14002	SEPA E	Devon	21	2002	0.996232	NO	0.868	0.299335588	Negative

14003	SEPA E	Allan	21	2001	0.999263	YES	0.898	0.332296773	Negative
14004	SEPA E	Teith	8	2001	0.965782	NO	0.924	0.536373832	Negative
14005	SEPA E	Forth	19	2000	0.999710	YES	0.919	0.453614497	Negative
14006	SEPA E	Carron	17	2001	0.998193	YES	0.956	0.405887807	Negative
14007	SEPA E	Avon	26	1997	0.999962	YES	-	0.544751223	Negative
14008	SEPA E	Almond	27	1997	0.999962	YES	0.661	0.803715025	Negative
14009	SEPA E	Water Of Leith	27	1997	0.989108	NO	0.909	0.239779006	Negative
14010	SEPA E	Esk	27	1989	0.999962	YES	0.883	0.287781186	Negative
14011	SEPA E	Tyne	27	1996	0.999287	YES	-	0.309991776	Negative
15001	SEPA E	Tweed	21	1990	0.999864	YES	-	0.619719666	Negative
15002	SEPA E	Whiteadder	22	1990	0.999917	YES	-	0.602062725	Negative
15003	SEPA E	Eye	22	1990	0.999904	YES	0.858	0.618143609	Negative
16001	SEPA W	Esk	24	1988	0.970597	NO	0.297	0.028325896	Positive
16002	SEPA W	Annan	22	1991	0.725857457	NO	0.696	0.212835671	Positive
16003	SEPA W	Nith	22	1990	0.997656	NO	0.737	0.274256315	Negative
16004	SEPA W	Urr Water	25	1990	0.996878	NO	0.813	0.189617938	Negative
16005	SEPA W	Dee	26	1992	0.999323	YES	0.959	0.455881314	Negative
16006	SEPA W	Cree	25	1990	0.999888	YES	0.878	0.541273487	Negative
16007	SEPA W	Water Of Luce	26	1988	0.998678	YES	0.888	0.297946038	Negative
17001	SEPA W	Clyde	31	1997	0.999623	YES	1	0.320033671	Negative
17002	SEPA W	Kelvin	28	1997	0.999927	YES	0.838	0.797382788	Negative
17003	SEPA W	White Cart	31	1988	0.999957	YES	0.797	0.461941796	Negative
17004	SEPA W	Black Cart	32	2001	0.999286	YES	0.752	0.693524276	Negative
17005	SEPA W	Leven	31	1988	0.998741	YES	0.892	0.06674191	No
17006	SEPA W	North Calder	29	1996	0.999979	YES	0.894	0.807582973	Negative
17007	SEPA W	South Calder	29	1997	0.999858	YES	0.676	0.435772005	Negative
17008	SEPA W	Ayr	26	1983	0.82653996	NO	0.272	0.16320608	Positive
17009	SEPA W	Irvine	29	1998	0.677684224	NO	0.424	0.186296272	Positive
17010	SEPA W	Annick	19	2000	0.963055	NO	0.252	0.170165679	Positive
17011	SEPA W	Garnock	27	2004	0.575627154	NO	0.407	0.191199833	Positive
17012	SEPA W	Lugton	28	2004	0.67207549	NO	0.212	0.171100729	Positive



*Tablo A1.2 Summary of TRP flux results for all sites*

HMS SiteID	Region ID	Name of River	Length of time series	Year before change	Probability of step change	Change point valid after familywise correction	Effect size of the step change	Actual size of the step change	Type of Trend
1001	NW	Mersey	35	2002	0.992249516	NO	0.764	0.134155299	Positive
1002	NW	Mersey	33	2001	0.998143258	NO	0.813	0.279389702	Positive
1003	NW	Irwell	35	2000	0.999520152	YES	0.505	0.359092672	Negative
1004	NW	Tame	33	1992	0.998021165	NO	0.595	0.127777639	Positive
1005	NW	Weaver	28	1993	0.987618324	NO	0.944	0.000953696	Positive
1006	NW	Alt	28	1990	0.999967875	YES	0.722	0.549491777	Negative
1007	NW	Ribble	32	1987	0.98876604	NO	0.666	0.008384112	Positive
1008	NW	Ribble	31	2002	0.959101837	NO	0.882	0.477713517	Positive
1009	NW	Calder	32	2002	0.960678074	NO	0.915	0.420063601	Positive
1010	NW	Wyre	22	1988	0.973328151	NO	0.888	0.147594545	Positive
1012	NW	Kent	24	1989	0.999823113	YES	0.934	0.602511573	Negative
1014	NW	Leven	26	1995	0.999664537	YES	0.343	0.576458971	Positive
1015	NW	Douglas	28	1996	0.80737145	NO	0.666	14.2849252	Positive
1016	NW	Darwen	30	1987	0.918600577	NO	0.972	0.093636726	Negative
1017	NW	Eden	25	1989	0.999900711	YES	0.767	0.690306965	Positive
1018	NW	Eamont	23	1990	0.998892104	YES	0.808	0.439922094	Negative
1019	NW	Eden	21	1985	0.969151409	NO	0.853	0.108341497	Positive
1020	NW	Esk	21	1987	0.99576529	NO	0.717	0.490612272	Negative
1021	NW	Lyne	17	1988	0.955789832	NO	0.843	0.233831962	No
1022	NW	Derwent	25	1988	0.998918377	YES	0.656	0.547646971	Negative
1023	NW	Lune	25	1988	0.976867647	NO	0.444	0.250155553	Negative
1024	NW	Beela	9	2007	0.655846213	NO	0.464	0.688018954	Negative
1025	NW	Eden	6	2007	0.943918673	NO	0.882	0.531098993	Negative
2001	NE	Tweed	20	2003	0.999558669	YES	0.772	0.687763217	Negative
2009	NE	Coquet	18	1998	0.981540991	NO	0.752	0.545196589	Negative
2012	NE	Wansbeck	20	2002	0.995512361	NO	0.882	0.443019152	Negative
2020	NE	North Tyne	18	1982	0.995190836	NO	0.626	0.616729916	Negative
2021	NE	South Tyne	22	2003	0.983085607	NO	0.646	0.84415053	Negative
2026	NE	Derwent	18	2002	0.966385156	NO	0.858	0.071817059	Positive
2044	NE	Wear	21	2002	0.99858541	YES	0.818	0.32792066	Positive
2058	NE	Tees	20	1988	0.996039673	NO	0.489	0.356878491	Positive
2061	NE	Tees	15	2003	0.837162092	NO	0.858	0.176945014	Positive
2923	NE	Tyne	21	1992	0.99524612	NO	0.707	0.480072509	Negative
3006	MI	Trent	30	1991	0.999936557	YES	0.909	0.390845159	Negative
3007	MI	Trent	35	2001	0.999954234	YES	0.757	0.490571633	Negative
3008	MI	Trent	29	1999	0.98311102	NO	-	0.24881302	Negative
3009	MI	Idle	27	1990	0.99994092	YES	0.868	0.383073761	Positive
3010	MI	Soar	23	1998	0.999699515	YES	0.863	0.416337312	Positive

3011	MI	Derwent	28	1990	0.999919457	YES	0.801	0.552688786	Positive
3012	MI	Stour	28	1997	0.99974332	YES	0.696	0.420847958	Positive
3013	MI	Tame	25	1999	0.998542923	YES	0.414	0.262487367	Negative
3014	MI	Sowe	26	1995	0.975118298	NO	0.878	0.030195898	Negative
3015	MI	Dove	25	1988	0.999921492	YES	0.747	0.434248126	Positive
3019	MI	Tern	26	1990	0.995018897	NO	0.717	0.123290317	Positive
3029	MI	Teme	27	1995	0.999349674	YES	0.787	0.279893411	Negative
3227	MI	Severn	28	1994	0.999305273	YES	0.924	0.37608882	Negative
3416	MI	Avon	29	1992	0.999989972	YES	0.742	0.641515795	Positive
3752	MI	Severn	26	1995	0.998089433	YES	0.919	0.422716179	Negative
4001	NE	Hull	19	2000	0.999528092	YES	0.934	0.670107997	Positive
4003	NE	Ouse	18	2000	0.998575032	YES	0.666	0.503596211	Negative
4004	NE	Aire	18	1997	0.992651473	NO	0.717	0.3193802	Negative
4005	NE	Aire	13	2004	0.988591228	NO	0.747	0.413195479	Negative
4006	NE	Calder	4	2008	0.932794487	NO	0.707	0.609749259	Positive
4007	NE	Don	13	2000	0.994114416	NO	0.595	0.429823852	Negative
4008	NE	Don	17	2000	0.842044836	NO	0.838	0.374938932	-
4009	NE	Dearne	14	2000	0.986678385	NO	0.656	0.079203256	Negative
4010	NE	Rother	13	2000	0.912579416	NO	0.828	0.212411645	Negative
4012	NE	Esk	11	2004	0.988891003	NO	0.823	0.753944467	Negative
4013	NE	Wharfe	18	2002	0.998786716	YES	0.888	0.492221968	Negative
4014	NE	Derwent	12	2004	0.996495986	YES	0.893	0.681914791	Positive
4015	NE	Ouse	16	2003	0.995797043	NO	0.404	0.534451078	Negative
5400	AN	Ancholme	1	2012	0.950212932	NO	-	-	Positive
5410	AN	Witham	7	2009	0.783596865	NO	0.767	0.328107609	Negative
5501	AN	Welland	8	2002	0.828026807	NO	0.525	1.25321335	Positive
5502	AN	Welland	15	2004	0.974819028	NO	0.989	0.53523942	No
5510	AN	Nene	16	1982	0.99883556	YES	0.929	0.737505793	Negative
5511	AN	Nene	13	1978	0.982707475	NO	0.823	0.544987454	No
5626	AN	Bedford Ouse	16	1984	0.998589595	YES	0.787	0.668908558	Positive
5651	AN	Ely Ouse	11	1984	0.887629116	NO	-	0.44206936	Negative
5683	AN	Mid Lev Main Dr	6	1982	0.967566759	NO	0.755	0.659021231	Positive
5714	AN	Wensum	17	1986	0.999377506	YES	0.712	0.705665972	Negative
5722	AN	Bure	17	1986	0.991123401	NO	0.863	0.311412464	Negative
5810	AN	Stour	18	1985	0.997718326	YES	0.853	0.466355885	Negative
5811	AN	Stour	18	1987	0.994449999	NO	0.853	0.968555174	Negative
5820	AN	Colne	17	2002	0.996488361	NO	1	0.829765239	Negative
5830	AN	Blackwater	13	1985	0.994114416	NO	-	0.798347805	Positive
5840	AN	Chelmer	17	1985	0.997469248	YES	0.925	0.551240831	Negative
6001	SE	Thames	21	2000	0.999719441	YES	0.666	0.529313892	Negative
6002	SE	Cherwell	16	2000	0.945919382	NO	0.909	0.321478163	Negative
6003	SE	Thame	17	1997	0.984271	NO	0.984	0.097666718	Negative

6004	SE	Kennett	25	1995	0.999938106	YES	0.823	0.647496381	Positive
6005	SE	Loddon	14	1985	0.9289874	NO	-	0.171036646	Negative
6006	SE	Thames	17	1993	0.999377506	YES	-	0.779848781	Negative
6007	SE	Colne	17	1997	0.997469248	YES	0.964	0.568307554	Negative
6008	SE	Wey	16	1997	0.999041277	YES	-	0.449486678	Negative
6009	SE	Mole	16	1993	0.999212824	YES	0.934	0.780632469	Negative
6010	SE	Thames	30	2001	0.999891202	YES	0.898	0.668198318	Negative
6101	SE	Lee	23	2002	0.999448482	YES	0.939	0.681392542	Negative
6102	SE	Lee	15	2002	0.996326707	NO	0.964	0.585885194	Positive
6104	SE	Lee	12	2002	0.992364906	NO	0.973	0.778970342	Negative
6105	SE	Lee	15	2000	0.992249516	NO	0.883	0.21662248	Negative
6106	SE	Roding	18	2000	0.995840898	NO	0.803	0.130041616	Positive
7001	SE	Medway	32	1995	0.999940068	YES	0.742	0.367086693	Negative
7002	SE	Eden	27	1995	0.999217831	YES	0.868	0.05857482	Negative
7003	SE	Great Stour	25	1994	0.9998237	YES	0.828	0.459808459	Positive
7004	SE	Rother	16	2002	0.963491209	NO	0.55	0.558160056	Positive
7005	SE	Cuckmere	28	2001	0.984848491	NO	0.868	0.568183309	Negative
7006	SE	Ouse	23	2002	0.999379022	YES	0.872	0.439987653	Negative
7007	SE	Rother	29	2002	0.999045062	YES	0.676	0.290634374	Negative
7008	SE	Arun	25	2002	0.956070501	NO	0.942	1.075901996	Negative
7011	SE	Blackwater	20	2001	0.997632011	YES	0.946	0.153555473	Negative
7012	SE	Test	23	2000	0.999905107	YES	0.979	0.653639742	Positive
7013	SE	Itchen	22	2002	0.999807796	YES	0.717	0.662134373	Positive
8001	SW	Avon	21	1995	0.991680188	NO	0.787	0.98016372	Positive
8002	SW	Somerset Frome	15	1995	0.986898126	NO	0.671	0.971845449	Negative
8003	SW	Midford Brook	22	1995	0.99590588	NO	0.813	0.969233604	Negative
8004	SW	Avon	23	1995	0.998759628	YES	0.878	0.895529481	Negative
8100	SW	Avon	18	1998	0.9996273	YES	0.696	0.947730147	Negative
8200	SW	Stour	8	1998	0.870187823	NO	0.878	0.619049337	Positive
8201	SW	Stour	11	2008	0.938786555	NO	0.632	0.892934052	Negative
8300	SW	Piddle	15	2004	0.939291203	NO	0.818	0.931419319	Negative
8326	SW	Tone	10	1983	0.793274538	NO	-	63.99188858	Negative
8400	SW	Frome	18	1995	0.998968966	YES	0.893	0.970979417	Positive
8426	SW	Parrett	19	1995	0.988068005	NO	0.449	0.971194565	Negative
9001	SW	Axe	26	2000	0.864664717	NO	0.767	0.16969946	Negative
9002	SW	Otter	29	1993	0.999938942	YES	0.777	0.406970705	No
9003	SW	Exe	18	1995	0.998786716	YES	0.54	0.332342111	Negative
9008	SW	Teign	21	1995	0.947363284	NO	0.823	0.039830529	Positive
9011	SW	Dart	21	1994	0.994669897	NO	0.813	0.266676156	Negative
9013	SW	Avon	18	1993	0.983721885	NO	0.671	0.246267931	Positive
9014	SW	Plym	29	1999	0.996177857	NO	0.757	0.305496688	Positive
9015	SW	Tavy	21	1985	0.988531497	NO	0.883	0.285571017	Positive

9017	SW	Tamar	32	1994	0.999893709	YES	0.616	0.363035897	Positive
9023	SW	Lynher	19	1999	0.98295711	NO	0.737	0.108443171	Negative
9024	SW	Fowey	19	1996	0.954600027	NO	0.848	0.179734972	Negative
9025	SW	Fal	32	1994	0.99981474	YES	0.752	0.061694439	Negative
9026	SW	Carnon	32	1986	0.9082974	NO	0.616	0.943476234	Negative
9027	SW	Camel	22	1994	0.96823896	NO	0.707	0.215255129	Negative
9028	SW	Torridge	19	1994	0.993628725	NO	0.747	0.280680607	Negative
9030	SW	Taw	21	1990	0.992542817	NO	0.383	0.392960351	Negative
9031	SW	Taw	9	2000	0.909282047	NO	0.671	0.15493864	Negative
9035	SW	Yeo	20	1993	0.988412834	NO	0.727	0.465980885	Positive
9036	SW	Exe	21	1987	0.976774935	NO	0.752	0.109792113	Negative
9037	SW	Red	26	1994	0.99645194	NO	0.686	0.149374484	Positive
10001	WA	Dee	16	2003	0.930686643	NO	0.823	0.355808513	Negative
10002	WA	Dee	27	1995	0.998534952	YES	0.737	0.492159733	Negative
10003	NW	Dee	23	2000	0.99704063	NO	0.813	0.330239911	Negative
10004	WA	Alwen	28	1995	0.997750652	NO	0.828	0.502910512	Positive
10005	WA	Clywedog	27	1988	0.999965652	YES	0.696	0.91911632	Negative
10006	WA	Alyn	22	2000	0.986008618	NO	0.757	0.203371348	Positive
10007	WA	Clwyd	25	2000	0.997407994	NO	0.727	0.117064758	Positive
10008	WA	Elwy	24	1998	0.989885144	NO	0.914	0.102689273	Positive
10009	WA	Ogmore	30	1993	0.999986041	YES	0.818	0.5961961	Positive
10010	WA	Neath	25	1992	0.999526978	YES	0.742	0.617473535	No
10011	WA	Ely	27	1999	0.997746426	NO	0.989	0.258220634	Negative
10012	WA	Taff	23	2000	0.999891733	YES	0.878	0.716195894	Positive
10013	WA	Rhymney	20	1983	0.996039673	NO	0.843	0.63487478	Negative
10014	WA	Dwyrdd	18	1995	0.861055987	NO	0.757	0.365630045	Negative
10015	WA	Dysynni	27	1992	0.992490109	NO	0.681	0.29032278	Negative
10016	WA	Gwyrffai	28	1992	0.998086116	NO	0.882	0.31722827	Negative
10017	WA	Dovey (Or Dyfi)	27	1995	0.999349674	YES	0.737	0.644696164	Negative
10018	WA	Wnion	17	1996	0.826976051	NO	0.737	0.259111326	Negative
10019	WA	Mawddach	19	1996	0.784881254	NO	0.545	0.204412688	Negative
10020	WA	Glaslyn	20	1995	0.832322751	NO	0.717	0.21589957	Negative
10021	WA	Dwyfawr	17	1998	0.90325147	NO	0.585	0.308365236	Negative
10022	WA	Ogwen	18	2001	0.957856156	NO	0.932	0.166017728	Positive
10023	WA	Conwy	29	1994	0.999708106	YES	0.914	0.668205018	Positive
10024	WA	Tawe	26	1996	0.999545024	YES	0.919	0.674940619	No
10025	WA	Loughor	19	2000	0.99897362	YES	0.409	0.566036174	No
10026	WA	Towy (Or Tywi)	23	1996	0.94359719	NO	0.838	0.266435194	Negative
10027	WA	Taf	26	1994	0.999253807	YES	0.727	0.235485298	Positive
10028	WA	Eastern Cleddau	15	1987	0.986898126	NO	0.484	0.391249014	Negative
10030	WA	Teifi	14	1998	0.820274848	NO	0.095	0.014311103	Negative
10032	WA	Rheidol	21	2006	0.812172733	NO	0.717	0.151838652	No

10033	WA	Usk	22	1994	0.998344581	YES	0.752	0.456333573	Negative
10034	WA	Afon Lwyd	20	1994	0.975347011	NO	0.55	0.296580808	No
10035	WA	Ebbw Fawr	16	1998	0.968149149	NO	0.595	0.293045953	Negative
10036	MI	Wye	18	1985	0.985673066	NO	0.858	0.442575565	Negative
10037	WA	Wye	31	1995	0.999746376	YES	0.828	0.362346202	Positive
10038	WA	Elan	17	1995	0.994358605	NO	0.883	0.663179952	Negative
10039	WA	Western Cleddau	24	1997	0.970597238	NO	0.444	0.081190776	Negative
10040	WA	Gwili	21	1998	0.926675709	NO	0.404	0.335151758	Negative
10041	WA	Ystwyth	17	2007	0.756568115	NO	0.151	0.390566147	Positive
10042	WA	Nant Y Fendrod	16	2006	0.423898022	NO	0.464	9.650044957	Positive
11001	SEPA N	Wick	26	1988	0.643314459	NO	0.217	1.429038136	Negative
11002	SEPA N	Shin	25	1995	0.746884075	NO	0.474	0.124764122	Positive
11003	SEPA N	Conon	26	1985	0.941760722	NO	0.414	0.383671597	Negative
11004	SEPA N	Beauly	22	1993	0.865416375	NO	0.621	0.159544951	Negative
11005	SEPA N	Ness	29	1993	0.952003302	NO	0.873	0.514147299	Negative
11006	SEPA N	Nairn	31	1985	0.996199093	NO	0.772	0.489449094	Negative
11007	SEPA N	Findhorn	31	1987	0.990217999	NO	0.333	0.083613879	Negative
11008	SEPA N	Lochy	24	1992	0.716464138	NO	0.606	0.836944021	Positive
11009	SEPA N	Carron	25	1987	0.894220654	NO	0.383	0.067003616	Positive
11010	SEPA N	Thurso	26	1988	0.681557372	NO	0.474	1.603339456	Negative
12001	SEPA N	Lossie	12	1999	0.756700367	NO	0.166	0.089279288	Negative
12002	SEPA N	Spey	17	2004	0.775708714	NO	0.727	0.028116707	Negative
12003	SEPA N	Deveron	9	1995	0.909282047	NO	0.851	0.190828907	Negative
12004	SEPA N	Ugie	15	1994	0.939291203	NO	0.207	0.070291087	Negative
12005	SEPA N	Ythan	18	1998	0.71724031	NO	0.808	0.318405698	Positive
12006	SEPA N	Don	13	1998	0.842556682	NO	0.694	0.467909532	Positive
12007	SEPA N	Dee	12	1981	0.96244885	NO	0.954	0.490877067	Negative
13001	SEPA E	Eden	25	2000	0.9994741	YES	0.984	0.512543219	Negative
13002	SEPA E	Earn	21	2000	0.99915856	YES	-	0.663763729	Negative
13003	SEPA E	Tay	28	2000	0.999967875	YES	1	0.747518539	Positive
13004	SEPA E	Dighty Water	21	2000	0.999864343	YES	0.954	0.679425809	Negative
13005	SEPA E	South Esk	23	2000	0.999214988	YES	0.954	0.646429599	Positive
13006	SEPA E	North Esk	23	2000	0.999510634	YES	0.828	0.719900612	Negative
14001	SEPA E	Leven	16	1995	0.979197918	NO	0.747	0.445375214	Negative
14002	SEPA E	Devon	21	2002	0.996232424	NO	0.863	0.227746914	Negative
14003	SEPA E	Allan	21	2002	0.998755386	YES	0.969	0.397797286	Negative
14004	SEPA E	Teith	8	2001	0.950728855	NO	0.828	0.491733679	Positive
14005	SEPA E	Forth	19	2000	0.999709781	YES	0.787	0.428145022	Negative
14006	SEPA E	Carron	17	2000	0.994358605	NO	0.944	0.353405612	Negative
14007	SEPA E	Avon	26	2000	0.99972711	YES	-	0.55450454	Negative
14008	SEPA E	Almond	27	1998	0.999926909	YES	0.752	0.778595228	Positive
14009	SEPA E	Water Of	27	1998	0.997102524	NO	0.752	0.586128169	Negative

		Leith							
14010	SEPA E	Esk	27	2000	0.996853035	NO	0.823	0.494124166	Negative
14011	SEPA E	Tyne	27	2000	0.998972835	YES	0.893	0.50107066	Negative
15001	SEPA E	Tweed	21	1988	0.999263321	YES	0.868	0.486935588	Negative
15002	SEPA E	Whiteadder	22	1988	0.999375269	YES	0.888	0.536422154	Negative
15003	SEPA E	Eye	22	1988	0.999626019	YES	0.631	0.695137319	Negative
16001	SEPA W	Esk	24	1988	0.963132197	NO	0.222	2.010221356	Negative
16002	SEPA W	Annan	22	1988	0.695967791	NO	0.752	1.03483598	Positive
16003	SEPA W	Nith	22	1991	0.984608087	NO	0.752	0.033127072	Negative
16004	SEPA W	Urr Water	25	1988	0.990261136	NO	0.878	0.096055848	Negative
16005	SEPA W	Dee	26	1992	0.998904526	YES	0.883	0.404100733	Negative
16006	SEPA W	Cree	25	1988	0.999202403	YES	0.742	0.503853	Negative
16007	SEPA W	Water Of Luce	26	1988	0.995790512	NO	0.727	0.363848813	Negative
17001	SEPA W	Clyde	31	2002	0.980438328	NO	0.939	0.306200956	Negative
17002	SEPA W	Kelvin	28	1992	0.999971071	YES	0.962	0.519699679	Positive
17003	SEPA W	White Cart	31	1990	0.99999098	YES	0.737	0.533869327	Negative
17004	SEPA W	Black Cart	32	2000	0.99292991	NO	0.922	0.372954864	Negative
17005	SEPA W	Leven	31	1993	0.999302233	YES	1	0.474204761	Negative
17006	SEPA W	North Calder	28	1993	0.999984741	YES	0.747	0.743007745	Negative
17007	SEPA W	South Calder	28	1990	0.999787289	YES	0.505	0.311139581	Positive
17008	SEPA W	Ayr	25	1983	0.672714721	NO	0.136	0.753640241	Negative
17009	SEPA W	Irvine	29	1993	0.575194415	NO	0.111	2.110447676	Negative
17010	SEPA W	Annick	19	2005	0.595452512	NO	0.257	0.209569377	Negative
17011	SEPA W	Garnock	27	2002	0.548340442	NO	0.419	0.619874089	Negative
17012	SEPA W	Lugton	28	2004	0.649156068	NO	0.191	0.098070534	Negative

*Tablo A2.3 Summary of TP concentration results for all sites*

HMS SiteID	Region ID	Name of River	Length of time series	Year before change	Probability of step change	Change point valid after familywise correction	Effect size of the step change	Actual size of the step change	Type of Trend
1001	NW	Mersey	8	2005	0.930517	NO	0.707	0.243	Negative
1002	NW	Mersey	9	2006	0.948334	NO	0.818	0.142	Negative
1003	NW	Irwell	8	2006	0.984496	NO	-	0.355	Negative
1004	NW	Tame	7	2005	0.968059	NO	0.858	0.342	Negative
1005	NW	Weaver	10	2011	0.829202	NO	-	0.233	Negative
1006	NW	Alt	6	2007	0.967567	NO	-	0.717	Negative
1007	NW	Ribble	7	2004	0.889648	NO	0.892	0.353	Negative
1008	NW	Ribble	11	2000	0.985468	NO	0.898	0.419	Negative
1009	NW	Calder	7	2005	0.924735	NO	0.868	0.659	Negative
1010	NW	Wyre	11	1995	0.907465	NO	0.939	0.277	Positive
1012	NW	Kent	16	2003	0.997948	YES	-	0.460	Negative
1014	NW	Leven	16	2006	0.997948	YES	0.979	0.377	Negative
1015	NW	Douglas	7	2006	0.924735	NO	0.949	0.367	Negative
1016	NW	Darwen	5	2005	0.632121	NO	0.762	0.126	Positive
1017	NW	Eden	13	2003	0.996309	YES	-	0.666	Negative
1018	NW	Eamont	14	2004	0.997397	YES	0.828	0.659	Negative
1019	NW	Eden	2	1975	0.864665	NO	-	0.526	Negative
1020	NW	Esk	10	2006	0.992621	NO	-	0.652	Negative
1021	NW	Lyne	7	2003	0.968059	NO	0.896	0.497	Negative
1022	NW	Derwent	10	2006	0.989819	NO	0.781	0.679	Negative
1023	NW	Lune	14	2004	0.972676	NO	0.747	0.204	Negative
1024	NW	Beela	10	2005	0.860416	NO	0.771	0.140	Positive
1025	NW	Eden	7	2007	0.968059	NO	0.893	0.343	Negative
2001	NE	Tweed	22	1996	0.999450	YES	-	0.496	Negative
2009	NE	Coquet	19	1998	0.999710	YES	-	0.566	Negative
2012	NE	Wansbeck	20	2002	0.999559	YES	0.803	0.604	Negative
2020	NE	North Tyne	23	1998	0.999215	YES	0.873	0.524	Negative
2021	NE	South Tyne	23	1997	0.999660	YES	0.979	0.451	Negative
2026	NE	Derwent	21	2004	0.999573	YES	0.949	0.626	Negative
2044	NE	Wear	17	1998	0.998928	YES	0.959	0.542	Negative
2058	NE	Tees	10	1981	0.981246	NO	-	0.348	Negative
2061	NE	Tees	14	2003	0.993916	NO	0.984	0.469	Negative
2923	NE	Tyne	22	1997	0.999626	YES	0.939	0.461	Negative
3006	MI	Trent	13	2005	0.996309	YES	0.922	0.404	Negative
3007	MI	Trent	16	2003	0.998836	YES	0.959	0.446	Negative
3008	MI	Trent	10	2002	0.992621	NO	0.949	0.366	Negative
3009	MI	Idle	12	2005	0.996496	YES	-	0.724	Negative
3010	MI	Soar	12	2004	0.995428	NO	-	0.467	Negative

3011	MI	Derwent	12	2006	0.996496	YES	0.969	0.698	Negative
3012	MI	Stour	15	2003	0.998916	YES	0.989	0.468	Negative
3013	MI	Tame	11	2000	0.985468	NO	0.929	0.481	Negative
3014	MI	Sowe	12	2004	0.994073	NO	0.929	0.379	Negative
3015	MI	Dove	11	2003	0.993667	NO	-	0.376	Negative
3019	MI	Tern	8	2002	0.984496	NO	-	0.242	Negative
3029	MI	Teme	10	2003	0.981246	NO	-	0.344	Negative
3227	MI	Severn	11	2006	0.995277	NO	0.989	0.366	Negative
3416	MI	Avon	15	2005	0.992250	NO	0.707	0.618	Negative
3752	MI	Severn	12	2005	0.984296	NO	0.767	0.120	Negative
4001	NE	Hull	9	2009	0.931029	NO	0.696	0.148	Negative
4003	NE	Ouse	8	2010	0.930517	NO	0.484	0.121	Negative
4004	NE	Aire	7	2011	0.624536	NO	0.297	0.053	Positive
4005	NE	Aire	7	2009	0.710557	NO	0.702	0.119	Positive
4006	NE	Calder	4	2011	0.932794	NO	-	0.437	Negative
4007	NE	Don	6	2007	0.907538	NO	0.888	0.163	Negative
4008	NE	Don	2	2007	0.864665	NO	-	0.114	Negative
4009	NE	Dearne	5	2005	0.763072	NO	0.329	0.079	Positive
4010	NE	Rother	5	2007	0.859142	NO	-	0.108	Positive
4012	NE	Esk	10	2004	0.928639	NO	0.893	0.465	Negative
4013	NE	Wharfe	9	2006	0.972268	NO	0.747	0.276	Negative
4014	NE	Derwent	8	2005	0.930517	NO	0.873	0.346	Negative
4015	NE	Ouse	9	2009	0.972268	NO	0.737	0.223	Negative
5400	AN	Ancholme	7	2011	0.624536	NO	0.545	0.074	Negative
5410	AN	Witham	8	2005	0.930517	NO	0.595	0.555	Negative
5500	AN	Welland	1	1975	0.950213	NO		-	
5501	AN	Welland	8	2003	0.984496	NO	-	0.594	Negative
5502	AN	Nene	11	2006	0.995277	NO	-	0.498	Negative
5510	AN	Nene	8	2007	0.984496	NO	0.898	0.538	Negative
5511	AN	Bedford Ouse	13	2005	0.997099	YES	0.838	0.730	Negative
5626	AN	Ely Ouse	8	2006	0.965782	NO	-	0.438	Negative
5651	AN	Mid Lev Main Dr	4	2005	0.932794	NO	-	0.417	Negative
5683	AN	Wensum	5	2005	0.922695	NO	0.77	0.447	Negative
5714	AN	Bure	10	2005	0.981246	NO	0.909	0.473	Negative
5722	AN	Stour	14	1999	0.986678	NO	1	0.991	Negative
5810	AN	Stour	9	2006	0.990242	NO	0.858	0.998	Negative
5811	AN	Colne	9	2007	0.980129	NO	0.878	0.999	Negative
5820	AN	Blackwater	13	2005	0.995327	NO	-	0.458	Negative
5830	AN	Chelmer	8	2005	0.984496	NO	0.914	0.998	Negative
5840	SE	Thames	10	2006	0.989819	NO	0.616	0.997	Negative
6001	SE	Cherwell	7	2006	0.783597	NO	0.878	0.328	Negative
6002	SE	Thame	4	2011	0.846645	NO	0.693	0.176	Negative



6003	SE	Kennett	6	2011	0.854644	NO	-	0.207	Negative
6004	SE	Loddon	7	2005	0.889648	NO	0.934	0.421	Negative
6005	SE	Thames	5	2005	0.922695	NO	-	0.234	Negative
6006	SE	Colne	8	2005	0.870188	NO	0.919	0.318	Negative
6007	SE	Wey	6	2005	0.907538	NO	-	0.398	Negative
6008	SE	Mole	7	2006	0.980126	NO	-	0.502	Negative
6009	SE	Thames	7	2009	0.980126	NO	0.636	0.453	Negative
6010	SE	Lee	6	2009	0.907538	NO	-	0.233	Negative
6101	SE	Lee	10	2006	0.986107	NO	0.797	0.689	Negative
6102	SE	Lee	6	2009	0.907538	NO	0.626	0.168	Negative
6104	SE	Lee	6	2005	0.967567	NO	0.747	0.688	Negative
6105	SE	Roding	9	2007	0.972268	NO	0.934	0.200	Negative
6106	SE	Medway	7	2009	0.968059	NO	0.954	0.328	Negative
7001	SE	Eden	15	2005	0.998349	YES	0.767	0.392	Negative
7002	SE	Great Stour	10	2007	0.944171	NO	0.818	0.103	Negative
7003	SE	Rother	11	2005	0.975742	NO	0.821	0.338	Negative
7004	SE	Cuckmere	14	2005	0.993916	NO	0.858	0.473	Negative
7005	SE	Ouse	9	2006	0.948334	NO	0.631	0.216	Negative
7006	SE	Rother	9	2007	0.909282	NO	0.959	0.153	Negative
7007	SE	Arun	9	2006	0.931029	NO	0.878	0.194	Negative
7008	SE	Blackwater	7	2007	0.968059	NO	0.868	0.707	Negative
7011	SE	Test	9	2008	0.961867	NO	0.727	0.152	Negative
7012	SE	Itchen	10	2008	0.981246	NO	-	0.365	Negative
7013	SW	Avon	10	2007	0.992621	NO	-	0.594	Negative
8001	SW	Somerset Frome	8	2005	0.984496	NO	0.969	0.480	Negative
8002	SW	Midford Brook	4	2005	0.932794	NO	0.747	0.377	Negative
8003	SW	Avon	9	2005	0.980129	NO	0.954	0.413	Negative
8004	SW	Avon	11	2005	0.995277	NO	0.828	0.588	Negative
8100	SW	Stour	10	2005	0.966929	NO	0.868	0.347	Negative
8200	SW	Stour	2	1998	0.864665	NO	-	0.000	Negative
8201	SW	Piddle	11	2006	0.981147	NO	0.727	0.181	Negative
8300	SW	Tone	11	2006	0.969045	NO	0.707	0.219	Negative
8326	SW	Frome	3	2004	0.930517	NO	-	0.436	Negative
8400	SW	Parrett	8	2006	0.984496	NO	-	0.416	Negative
8426	SW	Axe	12	2005	0.996496	YES	-	0.305	Negative
9001	SW	Otter	8	2005	0.984496	NO	-	0.556	Negative
9002	SW	Exe	9	2004	0.985972	NO	0.904	0.386	Negative
9003	SW	Teign	8	2004	0.976726	NO	-	0.276	Negative
9008	SW	Dart	6	2003	0.967567	NO	0.888	0.405	Negative
9011	SW	Avon	9	2005	0.961867	NO	0.727	0.260	Negative
9013	SW	Plym	6	2004	0.854644	NO	0.791	0.063	Negative
9014	SW	Tavy	12	2005	0.995428	NO	-	0.474	Negative

9015	SW	Tamar	11	2004	0.993667	NO	0.737	0.358	Negative
9017	SW	Lynher	13	2005	0.955243	NO	0.878	0.153	Negative
9023	SW	Fowey	11	2005	0.985468	NO	0.893	0.338	Negative
9024	SW	Fal	11	2006	0.985468	NO	-	0.372	Negative
9025	SW	Carnon	11	2005	0.993667	NO	0.823	0.357	Negative
9026	SW	Camel	13	2003	0.842557	NO	0.494	0.057	Positive
9027	SW	Torr ridge	13	2006	0.962618	NO	0.83	0.259	Negative
9028	SW	Taw	6	2003	0.967567	NO	-	0.311	Negative
9030	SW	Taw	7	2008	0.980126	NO	-	0.250	Negative
9031	SW	Yeo	5	2009	0.960836	NO	-	0.647	Negative
9035	SW	Exe	6	2004	0.943919	NO	-	0.432	Negative
9036	SW	Red	7	2007	0.980126	NO	0.656	0.456	Negative
9037	WA	Dee	15	2005	0.974819	NO	0.454	0.288	Positive
10001	WA	Dee	13	2006	0.767925	NO	0.974	0.175	Positive
10002	NW	Dee	14	2005	0.997916	YES	-	0.484	Negative
10003	WA	Alwen	11	2003	0.985468	NO	0.838	0.432	Negative
10004	WA	Clywedog	13	2004	0.968935	NO	0.848	0.181	Negative
10005	WA	Alyn	14	2004	0.992553	NO	0.808	0.936	Negative
10006	WA	Clwyd	11	2003	0.960823	NO	0.924	0.249	Negative
10007	WA	Elwy	10	2003	0.981246	NO	0.747	0.271	Negative
10008	WA	Ogmore	11	2009	0.938787	NO	0.949	0.171	Negative
10009	WA	Neath	10	2007	0.974960	NO	0.929	0.129	Negative
10010	WA	Ely	10	2006	0.928639	NO	0.545	0.211	Negative
10011	WA	Taff	8	2010	0.930517	NO	0.828	0.454	Negative
10012	WA	Rhymney	6	2010	0.782120	NO	0.691	0.010	Positive
10013	WA	Dwyrdd	6	2008	0.782120	NO	0.565	0.306	Positive
10014	WA	Dysynni	8	2006	0.776870	NO	0.696	0.130	Positive
10015	WA	Gwyrfa	10	2005	0.793275	NO	0.752	0.034	Positive
10016	WA	Dovey (Or Dyfi)	7	2005	0.889648	NO	0.712	0.196	Negative
10017	WA	Wnion	10	2007	0.656680	NO	0.267	0.082	Positive
10018	WA	Mawddach	8	2009	0.716464	NO	0.603	0.117	Negative
10019	WA	Glaslyn	9	2007	0.714025	NO	0.785	0.038	Positive
10020	WA	Dwyfawr	9	2008	0.961867	NO	0.868	0.550	Negative
10021	WA	Ogwen	9	2005	0.961867	NO	0.792	0.480	Negative
10022	WA	Conwy	8	2005	0.776870	NO	0.454	0.118	Negative
10023	WA	Tawe	8	2011	0.828027	NO	0.804	0.123	Positive
10024	WA	Loughor	10	2008	0.956796	NO	0.737	0.219	Negative
10025	WA	Towy (Or Tywi)	7	2008	0.843083	NO	0.242	0.085	Negative
10026	WA	Taf	9	2009	0.765864	NO	0.265	0.095	Positive
10027	WA	Eastern Cleddau	9	2010	0.523239	NO	0.146	0.111	Positive
10030	WA	Terfi	6	2010	0.575627	NO	0.823	0.069	Positive
10032	WA	Rheidol	9	2006	0.931029	NO	0.858	0.202	Negative

10033	WA	Usk	8	2008	0.965782	NO	0.383	0.198	Negative
10034	WA	Afon Lwyd	6	2011	0.575627	NO		-	Positive
10035	WA	Ebbw Fawr	6	2005	0.907538	NO	0.878	0.232	Negative
10036	MI	Wye	3	2006	0.930517	NO	-	0.327	Negative
10037	WA	Wye	8	2009	0.950729	NO	0.767	0.286	Positive
10038	WA	Elan	7	2006	0.710557	NO	0.515	0.307	Negative
10039	WA	Western Cleddau	9	2011	0.523239	NO	0.363	0.220	Positive
10040	WA	Gwili	8	2006	0.776870	NO	0.55	0.164	Positive
10041	WA	Ystwyth	10	2006	0.928639	NO	0.599	0.364	Negative
10042	WA	Nant Y Fendrod	10	2006	0.829202	NO	0.964	0.058	Positive
11001	SEPA N	Wick	15	1996	0.818530	NO	0.303	0.189	Positive
11002	SEPA N	Shin	12	1998	0.756700	NO	0.117	0.055	Positive
11003	SEPA N	Conon	15	2001	0.553657	NO	0.858	0.355	Positive
11004	SEPA N	Beaully	15	1993	0.520495	NO	0.616	0.270	Positive
11005	SEPA N	Ness	21	1993	0.744903	NO	0.303	0.046	Positive
11006	SEPA N	Nairn	17	2003	0.736403	NO	0.414	0.018	Positive
11007	SEPA N	Findhorn	16	2001	0.517763	NO	0.606	0.471	Positive
11008	SEPA N	Lochy	12	2010	0.722532	NO	0.686	0.093	Positive
11009	SEPA N	Carron	16	1993	0.606229	NO	0.474	0.246	Positive
11010	SEPA N	Thurso	13	2010	0.706943	NO	0.661	0.049	Positive
12001	SEPA N	Lossie	7	2000	0.889648	NO	-	0.129	Positive
12002	SEPA N	Spey	9	1999	0.909282	NO	0.676	0.164	Negative
12003	SEPA N	Deveron	5	2001	0.922695	NO	-	0.415	Negative
12004	SEPA N	Ugie	3	2000	0.930517	NO	-	0.251	Negative
12005	SEPA N	Ythan	8	2001	0.776870	NO	0.636	0.069	Positive
12006	SEPA N	Don	3	2000	0.776870	NO	-	0.362	Negative
12007	SEPA N	Dee	3	2009	0.776870	NO	-	0.137	Positive
13001	SEPA E	Eden	12	2003	0.992365	NO	0.878	0.451	Negative
13002	SEPA E	Earn	8	2005	0.976726	NO	0.939	0.333	Negative
13003	SEPA E	Tay	14	2004	0.980765	NO	0.954	0.276	Negative
13004	SEPA E	Dighty Water	12	2007	0.992365	NO	0.904	0.645	Negative
13005	SEPA E	South Esk	8	2004	0.930517	NO	0.878	0.483	Negative
13006	SEPA E	North Esk	9	2003	0.931029	NO	0.494	0.597	Negative
14001	SEPA E	Leven	21	2000	0.978924	NO	0.752	0.135	Negative
14002	SEPA E	Devon	24	2002	0.997758	YES	0.929	0.202	Negative
14003	SEPA E	Allan	21	2006	0.994031	NO	0.929	0.406	Negative
14004	SEPA E	Teith	5	2007	0.922695	NO	-	0.155	Negative
14005	SEPA E	Forth	21	2007	0.995246	NO	0.962	0.306	Negative
14006	SEPA E	Carron	20	2001	0.999408	YES	-	0.420	Negative
14007	SEPA E	Avon	20	2000	0.999824	YES	1	0.557	Negative
14008	SEPA E	Almond	18	2000	0.999627	YES	0.767	0.757	Negative
14009	SEPA E	Water Of	21	1998	0.976775	NO	0.717	0.149	Negative

		Leith							
14010	SEPA E	Esk	20	2001	0.997301	NO	0.888	0.309	Negative
14011	SEPA E	Tyne	20	2000	0.999210	YES	0.818	0.405	Negative
15001	SEPA E	Tweed	7	2005	0.968059	NO	0.883	0.285	Negative
15002	SEPA E	Whiteadder	10	2007	0.974960	NO	0.939	0.195	Negative
15003	SEPA E	Eye	12	2005	0.996496	YES	0.626	0.371	Negative
16001	SEPA W	Esk	8	2002	0.716464	NO	0.451	0.342	Positive
16002	SEPA W	Annan	7	1997	0.968059	NO	-	0.413	Negative
16003	SEPA W	Nith	10	2000	0.989819	NO	0.888	0.347	Negative
16004	SEPA W	Urr Water	10	2000	0.986107	NO	-	0.258	Negative
16005	SEPA W	Dee	10	1997	0.981246	NO	0.767	0.324	Negative
16006	SEPA W	Cree	11	1997	0.969045	NO	0.722	0.161	Negative
16007	SEPA W	Water Of Luce	10	2000	0.966929	NO	0.898	0.238	Negative
17001	SEPA W	Clyde	16	2003	0.998836	YES	-	0.516	Negative
17002	SEPA W	Kelvin	12	2002	0.994073	NO	0.994	0.768	Negative
17003	SEPA W	White Cart	16	2003	0.999041	YES	-	0.500	Negative
17004	SEPA W	Black Cart	14	2003	0.998338	YES	0.727	0.834	Negative
17005	SEPA W	Leven	13	2000	0.925487	NO	0.666	0.423	Positive
17006	SEPA W	North Calder	5	2009	0.922695	NO	-	0.219	Negative
17007	SEPA W	South Calder	9	2005	0.985972	NO	-	0.628	Negative
17008	SEPA W	Ayr	9	2004	0.972268	NO	0.55	0.225	Negative
17009	SEPA W	Irvine	13	2005	0.955243	NO	-	0.133	Negative
17010	SEPA W	Annick	12	2005	0.996496	YES	0.767	0.520	Negative
17011	SEPA W	Garnock	11	2004	0.975742	NO	0.858	0.246	Negative
17012	SEPA W	Lugton	11	2004	0.981147	NO	0.555	0.196	Negative

*Tablo A2.4 Summary of TP flux results for all sites*

HMS SiteID	Region ID	Name of River	Length of time series	Year before change	Probability of step change	Change point valid after familywise correction	Effect size of the step change	Actual size of the step change	Type of Trend
1001	NW	Mersey	8	2008	0.870187823	NO	0.676	0.023289113	Positive
1002	NW	Mersey	8	2006	0.984496146	NO	-	0.367118152	Negative
1003	NW	Irwell	8	2008	0.950728855	NO	-	0.64033299	Positive
1004	NW	Tame	7	2005	0.968059406	NO	-	0.249356505	Negative
1005	NW	Weaver	8	2010	0.965781882	NO	0.792	0.344197659	Negative
1006	NW	Alt	6	2007	0.967566759	NO	0.58	0.610242654	Negative
1007	NW	Ribble	7	2009	0.843083399	NO	-	0.715872447	Negative
1008	NW	Ribble	11	2002	0.938786555	NO	0.727	0.121550768	Positive
1009	NW	Calder	7	2010	0.924734596	NO	0.626	0.678933506	Negative
1010	NW	Wyre	11	2012	0.39346934	NO		-	Positive
1012	NW	Kent	16	2000	0.921853718	NO	0.555	0.170465842	Negative
1014	NW	Leven	16	2006	0.982050995	NO	0.565	0.39246856	Negative
1015	NW	Douglas	7	2007	0.924734596	NO	0.686	0.956494682	Negative
1016	NW	Darwen	5	2010	0.763072241	NO	0.622	0.438065829	Positive
1017	NW	Eden	13	2003	0.912579416	NO	0.787	0.10568014	Positive
1018	NW	Eamont	14	2007	0.977027775	NO	0.636	0.334558728	Negative
1019	NW	Eden	2	1975	0.864664717	NO	-	-	Negative
1020	NW	Esk	10	2009	0.887163813	NO	0.661	0.520461374	Negative
1021	NW	Lyne	7	2009	0.710556718	NO	0.7	0.219528685	Positive
1022	NW	Derwent	10	2006	0.92863873	NO	0.459	0.748474489	Negative
1023	NW	Lune	14	2007	0.840663139	NO	0.474	0.27351024	Positive
1024	NW	Beela	10	2007	0.544087578	NO	0.313	0.372460366	Positive
1025	NW	Eden	7	2007	0.843083399	NO	0.858	0.156530674	Negative
2001	NE	Tweed	22	1998	0.998139185	YES	0.797	0.510978887	Negative
2009	NE	Coquet	19	1999	0.98295711	NO	0.707	0.296144719	Negative
2012	NE	Wansbeck	20	2002	0.99730134	NO	0.666	0.554921668	Negative
2020	NE	North Tyne	23	1998	0.991940377	NO	0.53	0.408958714	Negative
2021	NE	South Tyne	23	2002	0.94359719	NO	0.646	0.166234679	Negative
2026	NE	Derwent	21	1996	0.998394207	YES	0.747	0.323438024	Negative
2044	NE	Wear	17	1998	0.950212932	NO	0.626	0.039131652	Positive
2058	NE	Tees	10	2000	0.909775525	NO	0.676	0.552141012	Positive
2061	NE	Tees	14	2000	0.9289874	NO	0.641	0.093822546	Positive
2923	NE	Tyne	21	1998	0.991680188	NO	0.952	0.318614127	Negative
3006	MI	Trent	13	2004	0.992624208	NO	0.959	0.453162582	Negative
3007	MI	Trent	16	2002	0.99883556	YES	0.838	0.345565967	Negative
3008	MI	Trent	10	2002	0.9749598	NO	0.949	0.450400449	Negative
3009	MI	Idle	12	2008	0.954046635	NO	0.898	0.884443687	Positive
3010	MI	Soar	12	2002	0.987572214	NO	-	0.306394943	Negative

3011	MI	Derwent	12	2006	0.992364906	NO	0.898	0.562551237	Negative
3012	MI	Stour	15	2004	0.996326707	NO	0.919	0.561114864	Negative
3013	MI	Tame	11	2006	0.993667014	NO	0.848	0.265243724	Negative
3014	MI	Sowe	12	2006	0.990227717	NO	0.792	0.430625706	Negative
3015	MI	Dove	11	2007	0.924426125	NO	0.611	0.004348646	Positive
3019	MI	Tern	8	2005	0.930516549	NO	0.42	0.222237445	Negative
3029	MI	Teme	10	2002	0.9749598	NO	0.974	0.499951204	Negative
3227	MI	Severn	11	2005	0.991577592	NO	0.72	0.438413745	Negative
3416	MI	Avon	15	2002	0.986898126	NO	0.606	0.510795421	Negative
3752	MI	Severn	11	2004	0.808504805	NO	0.303	0.148845736	Positive
4001	NE	Hull	8	2012	0.486582881	NO		-	Positive
4003	NE	Ouse	8	2009	0.647133919	NO	0.373	0.028131212	Positive
4004	NE	Aire	7	2009	0.527633447	NO	0.494	0.404410255	Positive
4005	NE	Aire	7	2012	0.527633447	NO		-	Positive
4006	NE	Calder	4	2010	0.932794487	NO	0.535	0.401776987	Negative
4007	NE	Don	5	2008	0.859141579	NO	0.358	0.197391753	Negative
4008	NE	Don	2	2007	0.864664717	NO		-	Negative
4009	NE	Dearne	5	2008	0.632120559	NO	0.474	0.012704753	Positive
4010	NE	Rother	5	2007	0.763072241	NO	0.744	0.512506052	Positive
4012	NE	Esk	10	2005	0.829201833	NO	0.363	0.046662184	Positive
4013	NE	Wharfe	8	2010	0.716464138	NO	0.474	0.291466709	Positive
4014	NE	Derwent	8	2005	0.77686984	NO	0.555	0.310626921	Negative
4015	NE	Ouse	9	2010	0.811124397	NO	0.646	0.225715025	Positive
5400	AN	Ancholme	7	2008	0.710556718	NO	0.792	0.70610933	Positive
5410	AN	Witham	7	2009	0.783596865	NO	0.616	0.158764125	Positive
5500	AN	Welland	1	1975	0.950212932	NO		-	
5501	AN	Welland	6	2008	0.907537524	NO	-	0.556013718	Positive
5502	AN	Nene	10	2008	0.981246289	NO	-	0.547690937	Negative
5510	AN	Nene	8	2008	0.984496146	NO	-	0.859937142	Negative
5511	AN	Bedford Ouse	10	2008	0.9749598	NO	0.717	0.490564323	Negative
5626	AN	Ely Ouse	7	2006	0.843083399	NO	0.55	0.684202105	Negative
5651	AN	Mid Lev Main Dr	2	2004	0.864664717	NO	-	-	Negative
5683	AN	Wensum	4	2006	0.846645033	NO	0.544	0.547482446	Negative
5714	AN	Bure	10	2008	0.981246289	NO	0.752	0.755618858	Negative
5722	AN	Stour	10	2008	0.956795827	NO	-	0.44142825	Negative
5810	AN	Stour	8	2004	0.965781882	NO	-	0.593343031	Negative
5811	AN	Colne	8	2008	0.984496146	NO	0.915	0.80141973	Negative
5820	AN	Blackwater	12	1984	0.980283157	NO	0.454	0.516049469	Negative
5830	AN	Chelmer	5	2008	0.763072241	NO	0.843	0.25475772	Negative
5840	SE	Thames	10	1999	0.909775525	NO	0.737	0.960331618	Negative
6001	SE	Cherwell	7	2008	0.924734596	NO	0.772	0.211099224	Negative
6002	SE	Thame	4	2008	0.698805788	NO	0.707	0.522166741	Negative

6003	SE	Kennett	6	2010	0.907537524	NO	0.686	0.684240561	Positive
6004	SE	Loddon	7	2009	0.968059406	NO	0.656	0.668840707	Negative
6005	SE	Thames	4	2005	0.846645033	NO	-	0.472694654	Negative
6006	SE	Colne	8	2009	0.828026807	NO	0.626	0.059194207	Positive
6007	SE	Wey	6	2010	0.907537524	NO	-	0.54627785	Positive
6008	SE	Mole	7	2008	0.968059406	NO	-	0.404256818	Negative
6009	SE	Thames	7	2009	0.968059406	NO	0.868	0.546131732	Negative
6010	SE	Lee	6	2008	0.907537524	NO	0.893	0.33554248	Negative
6101	SE	Lee	10	2007	0.944170593	NO	0.656	0.65590121	Negative
6102	SE	Lee	6	2010	0.782119716	NO	0.55	0.028189207	Positive
6104	SE	Lee	5	2005	0.859141579	NO	0.333	0.693134305	Negative
6105	SE	Roding	9	2006	0.909282047	NO	0.757	0.197962487	Negative
6106	SE	Medway	7	2009	0.889648178	NO	0.636	0.22352307	Negative
7001	SE	Eden	14	1988	0.9289874	NO	0.575	0.232312049	Negative
7002	SE	Great Stour	9	2008	0.849876396	NO	0.585	0.067892769	Negative
7003	SE	Rother	10	1987	0.956795827	NO	0.767	0.518114449	Negative
7004	SE	Cuckmere	10	2008	0.966928749	NO	0.767	0.673054988	Negative
7005	SE	Ouse	9	2008	0.948334393	NO	0.873	0.606458042	Negative
7006	SE	Rother	9	2009	0.980129489	NO	0.909	0.716759825	Negative
7007	SE	Arun	8	2005	0.77686984	NO	0.843	0.136926809	Positive
7008	SE	Blackwater	5	2008	0.960836105	NO	-	0.957485571	Negative
7011	SE	Test	8	2005	0.904032914	NO	0.595	0.664815673	Negative
7012	SE	Itchen	8	2008	0.930516549	NO	-	0.33893067	Negative
7013	SW	Avon	9	2008	0.990241627	NO	0.646	0.647007344	Negative
8001	SW	Somerset Frome	7	2000	0.889648178	NO	0.777	0.404586558	Negative
8002	SW	Midford Brook	3	2005	0.930516549	NO	-	0.644807526	Negative
8003	SW	Avon	8	2000	0.904032914	NO	-	0.159708384	Positive
8004	SW	Avon	11	2005	0.969044563	NO	0.626	0.594671744	Negative
8100	SW	Stour	10	2008	0.92863873	NO	0.626	0.218609454	Negative
8200	SW	Stour	2	1998	0.864664717	NO	-	0.765806076	Negative
8201	SW	Piddle	9	2008	0.931029339	NO	0.639	0.332445882	Positive
8300	SW	Tone	10	2007	0.944170593	NO	0.888	0.277874505	Negative
8326	SW	Frome	3	2003	0.77686984	NO	0.464	0.140649014	Negative
8400	SW	Parrett	7	2009	0.950212932	NO	0.707	0.445084777	Negative
8426	SW	Axe	12	2008	0.918960656	NO	0.828	0.072897472	Positive
9001	SW	Otter	7	2005	0.968059406	NO	-	0.852709606	Negative
9002	SW	Exe	9	2004	0.972268468	NO	0.803	0.398722834	Negative
9003	SW	Teign	6	2003	0.967566759	NO	-	0.39045339	Negative
9008	SW	Dart	6	2003	0.943918673	NO	0.797	0.825497627	Negative
9011	SW	Avon	8	2008	0.870187823	NO	0.959	0.803589997	Negative
9013	SW	Plym	6	2010	0.688596776	NO	0.429	5.075658843	Positive
9014	SW	Tavy	11	2005	0.985468041	NO	0.934	0.798580269	Negative

9015	SW	Tamar	10	2004	0.986106909	NO	-	0.576650198	Negative
9017	SW	Lynher	12	2002	0.975402936	NO	0.808	0.689428283	Negative
9023	SW	Fowey	11	2003	0.950826317	NO	0.767	0.426254498	Negative
9024	SW	Fal	9	2002	0.948334393	NO	-	0.56097867	Negative
9025	SW	Carnon	10	2005	0.981246289	NO	0.803	0.511685194	Negative
9026	SW	Camel	11	2000	0.652798939	NO	0.611	0.116050934	Positive
9027	SW	Torr ridge	12	2005	0.903338342	NO	0.696	0.010565988	Positive
9028	SW	Taw	6	2008	0.943918673	NO	-	0.759910491	Negative
9030	SW	Taw	7	2008	0.980126485	NO	0.818	0.438248394	Negative
9031	SW	Yeo	4	2009	0.932794487	NO	-	0.652645616	Negative
9035	SW	Exe	5	2008	0.92269526	NO	-	0.749696549	Negative
9036	SW	Red	6	2007	0.967566759	NO	0.494	0.582281371	Negative
9037	WA	Dee	12	2009	0.865097789	NO	0.494	0.23666972	Positive
10001	WA	Dee	13	2009	0.767924645	NO	0.767	0.511302102	Positive
10002	NW	Dee	14	2009	0.961814756	NO	0.929	0.401466381	Negative
10003	WA	Alwen	11	2004	0.950826317	NO	0.626	0.036922794	Negative
10004	WA	Clywedog	13	2004	0.881484727	NO	0.747	0.44437591	Positive
10005	WA	Alyn	14	2006	0.983959733	NO	0.767	0.844946344	Negative
10006	WA	Clwyd	11	2009	0.975741987	NO	0.898	0.392658902	Positive
10007	WA	Elwy	10	2007	0.986106909	NO	0.752	0.264924779	Negative
10008	WA	Ogmore	11	2009	0.950826317	NO	0.494	0.640310837	Positive
10009	WA	Neath	9	2008	0.811124397	NO	0.474	0.008486855	Positive
10010	WA	Ely	9	2008	0.849876396	NO	0.555	0.0958975	Positive
10011	WA	Taff	8	2009	0.904032914	NO	0.494	0.3907304	Positive
10012	WA	Rhymney	6	2008	0.782119716	NO	0.111	0.19762379	Negative
10013	WA	Dwyrdd	6	2008	0.782119716	NO	0.616	0.439169486	Positive
10014	WA	Dysynni	8	2007	0.828026807	NO	0.075	0.037165296	Positive
10015	WA	Gwyrfa	10	2010	0.544087578	NO	0.5	2.486606809	Positive
10016	WA	Dovey (Or Dyfi)	7	2008	0.843083399	NO	0.813	0.339149112	Negative
10017	WA	Wnion	10	2007	0.793274538	NO	0.202	0.407796323	Positive
10018	WA	Mawddach	8	2009	0.486582881	NO	0.08	0.472954504	Positive
10019	WA	Glaslyn	9	2009	0.655846213	NO	0.676	0.124835491	Positive
10020	WA	Dwyfawr	9	2006	0.985971533	NO	-	0.826608298	Negative
10021	WA	Ogwen	9	2005	0.961866673	NO	0.515	0.693663793	Negative
10022	WA	Conwy	8	2007	0.950728855	NO	0.59	0.219920571	Negative
10023	WA	Tawe	8	2009	0.870187823	NO	0.464	0.445603476	Positive
10024	WA	Loughor	9	2011	0.655846213	NO	0.303	0.416549065	Positive
10025	WA	Towy (Or Tywi)	6	2009	0.782119716	NO	0.09	0.473857492	Negative
10026	WA	Taf	8	2009	0.486582881	NO	0.191	0.437052992	Positive
10027	WA	Eastern Cleddau	8	2009	0.716464138	NO	0.292	0.044346565	Positive
10030	WA	Terfi	5	2011	0.632120559	NO		-	Positive
10032	WA	Rheidol	8	2006	0.870187823	NO	0.565	0.113164826	Positive



10033	WA	Usk	7	2008	0.889648178	NO	0.898	0.680571574	Positive
10034	WA	Afon Lwyd	4	2006	0.698805788	NO	0.441	0.273186987	Positive
10035	WA	Ebbw Fawr	6	2007	0.907537524	NO	-	0.635919983	Positive
10036	MI	Wye	2	2005	0.864664717	NO	-	0.548464711	Negative
10037	WA	Wye	8	2009	0.950728855	NO	-	0.763384702	Negative
10038	WA	Elan	6	2009	0.967566759	NO	0.388	0.269221726	Negative
10039	WA	Western Cleddau	8	2011	0.569905359	NO	0.171	0.812202499	Positive
10040	WA	Gwili	7	2006	0.843083399	NO	0.398	0.041534301	Positive
10041	WA	Ystwyth	9	2007	0.811124397	NO	0.575	0.520958833	Positive
10042	WA	Nant Y Fendrod	9	2006	0.765863699	NO	0.494	0.259379392	Positive
11001	SEPA N	Wick	15	2010	0.617107114	NO	0.505	0.566622177	Positive
11002	SEPA N	Shin	12	1998	0.842156911	NO	0.393	0.579009096	Positive
11003	SEPA N	Conon	14	1997	0.876287619	NO	0.833	0.289137836	Positive
11004	SEPA N	Beaully	14	1993	0.947499825	NO	0.853	0.283233009	Negative
11005	SEPA N	Ness	21	1993	0.875119225	NO	0.575	0.175653285	Positive
11006	SEPA N	Nairn	17	1996	0.892792312	NO	0.454	0.281372167	Positive
11007	SEPA N	Findhorn	16	2001	0.796837677	NO	0.696	0.042012495	Positive
11008	SEPA N	Lochy	12	2011	0.466451407	NO	0.262	0.18365863	Positive
11009	SEPA N	Carron	16	1995	0.848536118	NO	0.707	0.053227552	Positive
11010	SEPA N	Thurso	13	2010	0.795042678	NO	0.363	0.205934616	Positive
12001	SEPA N	Lossie	7	2000	0.889648178	NO	-	0.214320005	Positive
12002	SEPA N	Spey	9	2009	0.931029339	NO	0.828	0.495117581	Negative
12003	SEPA N	Deveron	5	2001	0.92269526	NO	0.464	0.662624229	Positive
12004	SEPA N	Ugie	3	2000	0.77686984	NO	0.449	0.437652011	Positive
12005	SEPA N	Ythan	8	2001	0.870187823	NO	0.303	0.289484939	Positive
12006	SEPA N	Don	3	2009	0.77686984	NO	-	-	Positive
12007	SEPA N	Dee	3	2009	0.77686984	NO	-	0.319797212	Positive
13001	SEPA E	Eden	12	2001	0.980283157	NO	0.686	0.466756087	Negative
13002	SEPA E	Earn	8	2005	0.904032914	NO	0.939	0.226550217	Negative
13003	SEPA E	Tay	14	2006	0.992553417	NO	0.823	0.479208356	Negative
13004	SEPA E	Dighty Water	12	2007	0.975402936	NO	0.767	0.728211914	Negative
13005	SEPA E	South Esk	7	2007	0.783596865	NO	0.934	0.130958168	Negative
13006	SEPA E	North Esk	9	2000	0.765863699	NO	0.691	0.626520853	Negative
14001	SEPA E	Leven	15	2000	0.909884822	NO	0.56	0.134687303	Negative
14002	SEPA E	Devon	21	2000	0.974438467	NO	0.797	0.101060284	Negative
14003	SEPA E	Allan	18	2007	0.957856156	NO	0.656	0.354333465	Positive
14004	SEPA E	Teith	4	2008	0.932794487	NO	-	0.352865889	Negative
14005	SEPA E	Forth	19	2007	0.966755905	NO	0.671	0.274704261	Negative
14006	SEPA E	Carron	18	2000	0.976401891	NO	0.949	0.275296251	Negative
14007	SEPA E	Avon	18	2000	0.999374646	YES	-	0.554144471	Negative
14008	SEPA E	Almond	17	2000	0.999483003	YES	0.53	0.720653846	Negative
14009	SEPA E	Water Of Leith	19	2000	0.938919821	NO	0.681	0.45389335	Negative

14010	SEPA E	Esk	18	2000	0.988966538	NO	0.717	0.626916778	Negative
14011	SEPA E	Tyne	18	2001	0.992651473	NO	0.555	0.638584368	Negative
15001	SEPA E	Tweed	7	2005	0.950212932	NO	0.691	0.673789674	Positive
15002	SEPA E	Whiteadder	9	2009	0.765863699	NO	0.508	2.324022259	Positive
15003	SEPA E	Eye	11	2005	0.808504805	NO	0.585	0.095298244	Positive
16001	SEPA W	Esk	8	1997	0.828026807	NO	0.74	1.845750605	Positive
16002	SEPA W	Annan	7	1997	0.968059406	NO	0.861	0.569587306	Negative
16003	SEPA W	Nith	10	2002	0.956795827	NO	0.904	0.381847096	Negative
16004	SEPA W	Urr Water	10	2000	0.981246289	NO	0.873	0.521414287	Negative
16005	SEPA W	Dee	10	2000	0.92863873	NO	0.521	0.188203647	Negative
16006	SEPA W	Cree	11	2000	0.938786555	NO	0.904	0.266805843	Negative
16007	SEPA W	Water Of Luce	10	2002	0.981246289	NO	0.882	0.68691695	Negative
17001	SEPA W	Clyde	16	2004	0.995006571	NO	0.898	0.633896907	Negative
17002	SEPA W	Kelvin	11	2002	0.924426125	NO	0.878	0.457159527	Negative
17003	SEPA W	White Cart	15	2004	0.998915533	YES	-	0.451764667	Negative
17004	SEPA W	Black Cart	13	2004	0.997731774	YES	0.691	0.808419538	Negative
17005	SEPA W	Leven	13	2006	0.863053601	NO	0.777	0.117055626	Positive
17006	SEPA W	North Calder	5	2009	0.763072241	NO	0.505	0.471074926	Positive
17007	SEPA W	South Calder	8	2005	0.950728855	NO	0.747	0.490697267	Negative
17008	SEPA W	Ayr	8	2004	0.930516549	NO	0.515	0.197066827	Negative
17009	SEPA W	Irvine	12	2005	0.903338342	NO	0.944	0.149501278	Positive
17010	SEPA W	Annick	11	2006	0.985468041	NO	0.41	0.551002717	Negative
17011	SEPA W	Garnock	11	2004	0.887629116	NO	0.313	0.059960881	Positive
17012	SEPA W	Lugton	6	2004	0.782119716	NO	-	0.180623025	Positive